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THE
CHEMICAL ASPECTS
OF
LIGHT

BY
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FELLOW OF UNIVERSITY COLLEGE
OXFORD

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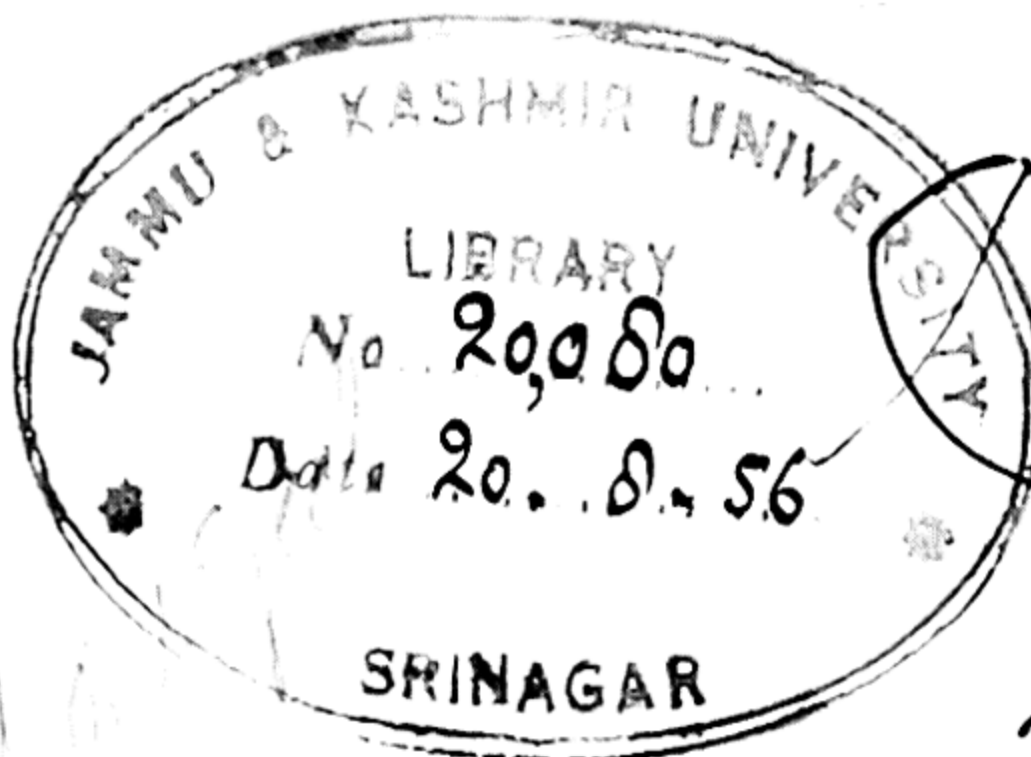


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PREFACE

THE second edition of this book has the same aim as the first: to present modern ideas of matter and light as far as possible in a non-mathematical form. Much of the text has been rewritten, partly to correct errors, but chiefly to replace the 'particle' concept of electrons in atoms by the 'wave' concept. Wave-mechanics is a difficult subject which cannot by its intrinsic nature be conveyed in a pictorial form, yet such a theoretically unsound task is what is attempted here. So long as the resulting limitations are kept in mind it is better to have a useful but imperfect tool adapted to the chemist's purposes than the pure truth in an unusable form. The treatment is deliberately extensive rather than intensive, and is intended to supplement rather than to replace existing text-books and articles. It is hoped that the reader will not find the result *lucus a non lucendo*.

OXFORD

E. J. B.

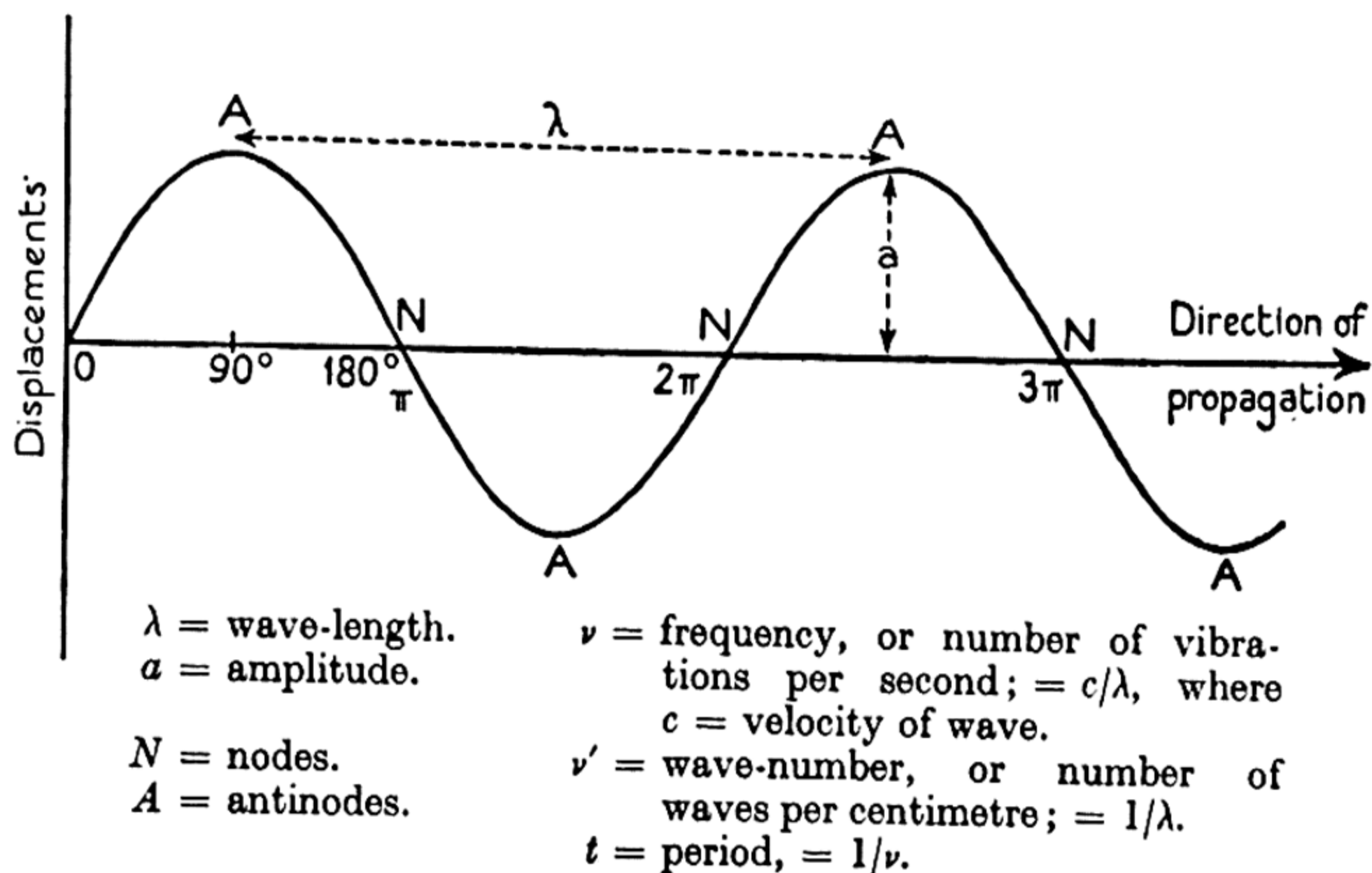
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I

LIGHT AS WAVES

'We all know what light is, but it is not easy to tell *what* it is.' The force of this remark of Dr. Johnson's is not likely to be diminished by the advances of knowledge. Scientists content themselves with interpretations of the properties of



Phase = angle whose sine gives the displacement at any point.
 Intensity of energy in wave varies as a^2 .

FIG. 1

light by using models; regarding it sometimes as a collection of particles, sometimes as waves. It is the latter aspect with which this chapter deals. Light has been found to travel at the constant rate of about 3×10^{10} cm./sec. *in vacuo*, and its behaviour when travelling may be visualized in terms of idealized transverse waves. A *plane or linearly polarized* train of transverse waves, i.e. one in which the displacements are confined to one plane and are at right angles to the direction of travel, is graphically represented in Fig. 1. Radiation in which the waves are all sensibly of the same frequency is called 'monochromatic'. Other types of transverse waves,

circularly and *elliptically* polarized, are those in which the displacements, viewed along the direction of the wave train, are circular or elliptical instead of linear. A circularly polarized wave may be regarded as compounded of two equal linearly polarized waves with displacements at right angles to each other and differing in phase by $\frac{1}{2}\pi$, i.e. one retarded behind the other by a quarter wave-length. More generally, waves linearly polarized at right angles to each other and different in phase compound into elliptically polarized waves. Wave motion implies a medium, and the hypothetical medium in which the waves 'exist' has been called the 'ether', but it is now realized that it is more satisfactory to regard it as sufficient that the mathematical representation of radiations in terms of idealized wave motion is capable of accounting for many of their properties, and to put aside attempts to visualize the nature of the 'ether' in relation to that of material bodies. The *electromagnetic theory* of Maxwell assumes that the displacements forming the wave trains of radiation are of the nature of alternating electrical currents with their associated magnetic effects. There results an electric and a magnetic vector at right angles to each other and to the direction of travel of the wave. The electric vector is the one on which attention is commonly fixed, and the polarization of a light-wave can be referred to the direction of this vector quantity. The 'plane of polarization' as defined by early physicists, however, happens to be that of the magnetic vector, so that care must be exercised in making quite clear what plane is used as a reference in any problem. Fig. 2 shows diagrammatically the way we can visualize the 'electric disturbance' caused by the passage of a wave past a point, looking along the direction of travel. It represents for example how the electric vector distorts the 'electronic structure' of an atom in a simple example.

The theory is mathematically expressed as a set of differ-

ential equations, the solutions to which under appropriate boundary conditions account for a wide range of the properties of radiation. Like all theories expressed in differential

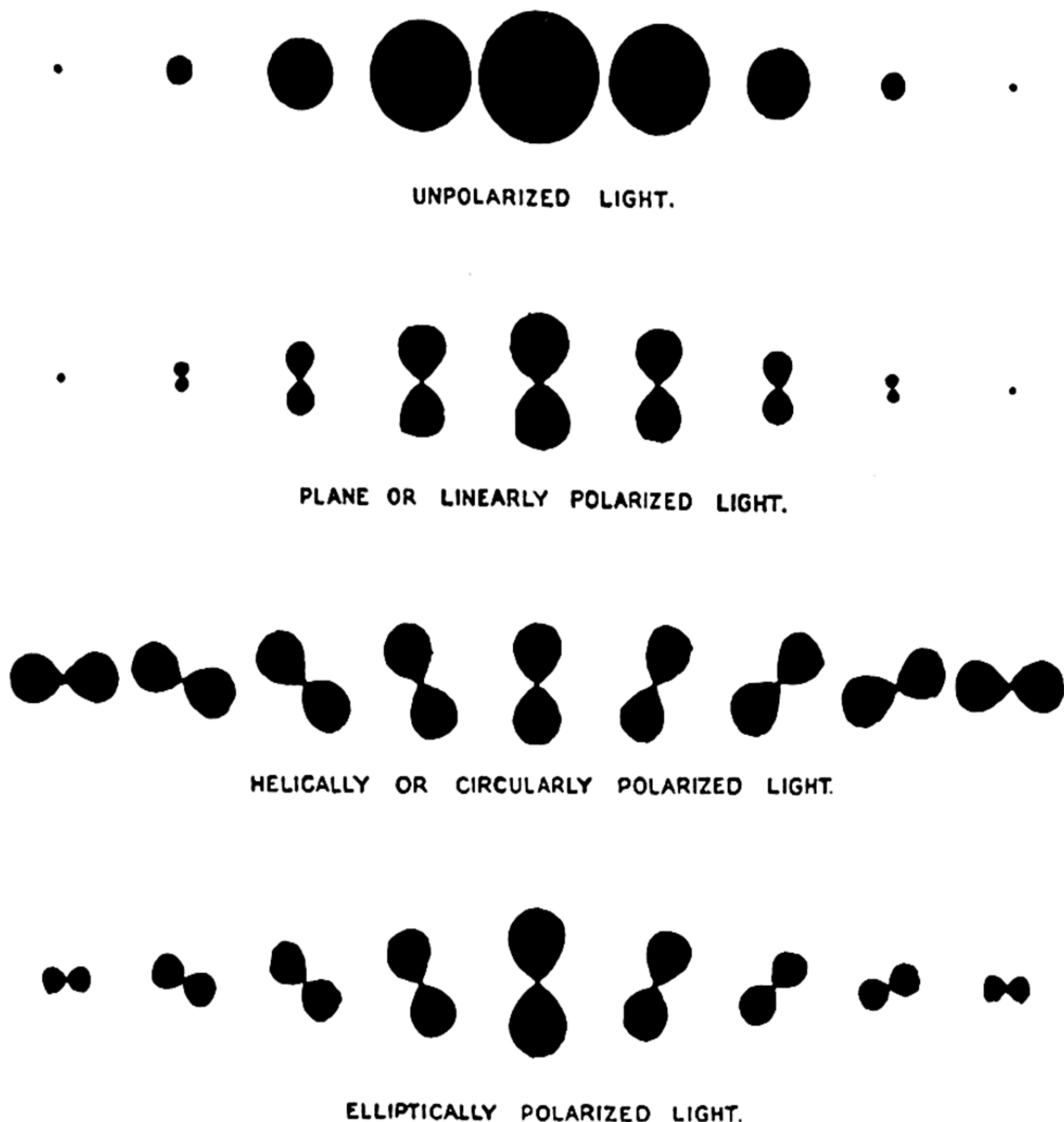


FIG. 2. Successive end-on views at equal time intervals of one half of a wavelength of a light wave. The black regions represent in polar coordinates the intensity of the light along various angles in the plane of the paper as it travels and is viewed normal to the paper.

form, it depends for its elegance and economy on the simplicity of its fundamental equations, and translation of its concepts into 'models' is effected only with the loss of its rigour and generality. In the range of phenomena of transmission, reflection, and refraction it appears capable of inter-

preting the most complex effects, the only difficulties being purely mathematical ones involved in the solution of the equations under the fixed conditions of the problem. These difficulties can only be surmounted by a mastery of the mathematical technique by a thorough training in the theory of differential equations.

The *electronic theory of matter* regards atoms as composed of minute positively charged nuclei surrounded by negative electrons. The electric displacements of the Maxwell waves are imagined as interacting with electrons or nuclei to produce the effect of matter on radiations. This method of treatment proves very satisfactory if radiation is not *absorbed* or *emitted*. Phenomena involving these processes need the additional assumptions of the Quantum Theory. The fundamental law of this theory is that energy in the form of radiation is absorbed or emitted only in *quanta* of magnitude $E = h\nu$, where E is the energy, ν the frequency of the radiation, and h is Planck's constant, 6.62×10^{-27} erg sec. Radiation therefore appears in a dual nature, that represented by electromagnetic waves and that more like the concept of a particle, i.e. as a quantum or bundle of energy of fixed amount. A light quantum is sometimes referred to as a '*photon*'.† Observations on radiation which require the quantum theory for interpretation are discussed in Chapter III.

The quantum equation, $E = h\nu = hc/\lambda$, enables us to express energy, usually measured in ergs, calories, joules, or electron volts (voltage through which the electronic charge e must drop to gain equivalent energy), in a number of other ways, as frequency, wave-number, wave-length, or kilogram calories per gram molecule. (See p. 295.) The magnitude of a quantum of energy of wave-length 3,000 Å, of frequency 10^{15} sec.⁻¹, and wave-number 3.333×10^4 cm.⁻¹, is 6.62×10^{-12}

† The term *photon* is also used in another connexion: as a unit of retinal illumination in experiments on the sensitivity of the eye.

ergs, 1.584×10^{-19} calories, or 4.11 electron volts. All these numerical values are equivalent. In chemistry the 'gram molecule' (6.023×10^{23} molecules) is more often used as a unit instead of a single molecule. A gram molecular number of the above quanta is equal to 95.27 kilogram calories. Radiations of a very wide range of frequencies or wave-lengths are known and are shown diagrammatically in Fig. 3. It can be seen by referring to the figure that the magnitude of a 'gram molecule' of quanta of γ -rays is about 10^7 , of X-rays about

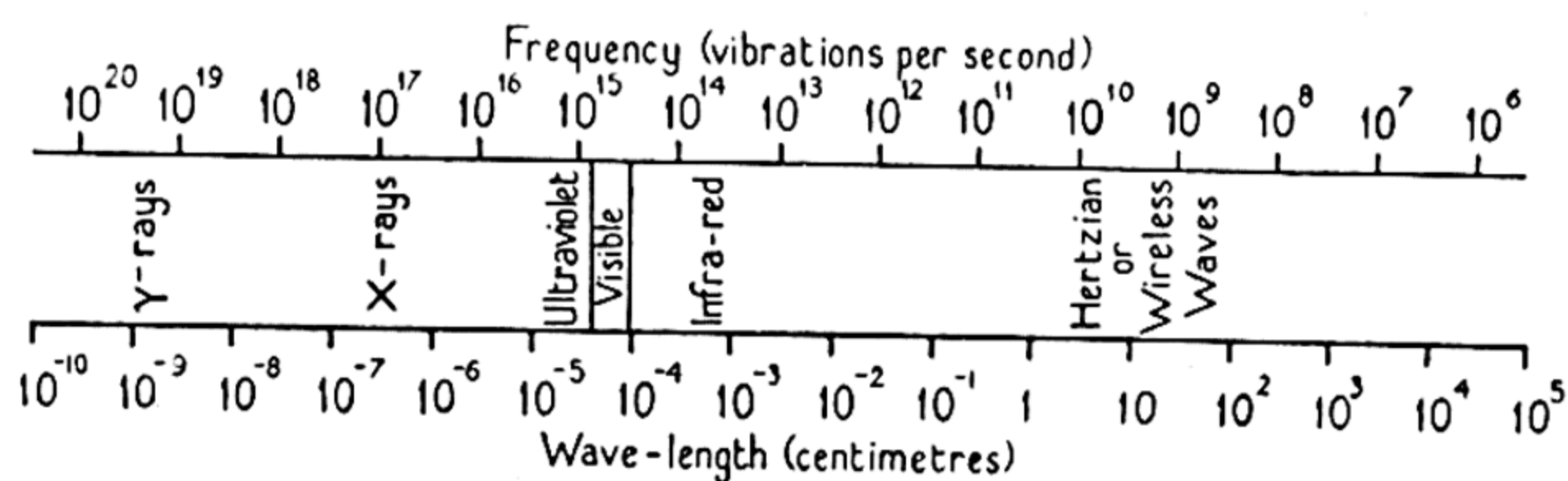


FIG. 3

10^5 , of ultra-violet or visible rays about 10^3 , of near infra-red about 10^2 , of far infra-red about 10, and of wireless waves 10^{-3} – 10^{-6} kilogram calories. These radiations of widely different energies are emitted or absorbed by matter in very different ways. γ -rays (frequency 10^{19} – 10^{20} per sec.) arise from changes in the energy levels of the nuclei of atoms, involving atomic transformations; X-rays (10^{16} – 10^{18} per sec.) from the inner electron shells of atoms; ultra-violet or visible rays (about 10^{15} per sec.) from electrons in the outer shells; near infra-red rays (10^{13} – 10^{14} per sec.) from the vibrations of atoms bound together as molecules, far infra-red rays (10^{12} – 10^{13} per sec.) from the rotations of molecules; and wireless waves (10^6 – 10^{10} per sec.) from the oscillations of electrons set up in closed electrical circuits of comparatively large size. From the chemical point of view the ultra-violet and visible region is of the greatest interest, as chemical changes are concerned with the outer electrons of atoms and molecules, and the absorption of such light may bring about

photochemical reactions. Second in interest is the infra-red region, since from a study of the vibrations and rotations of molecules their interatomic distances, angles, and force constants may be determined. The term *light*, strictly referring to visible radiations, is more conveniently extended to include the ultra-violet region, and, for certain purposes, the near infra-red region besides.

A characteristic feature of wave motion is *interference*, arising from the superposition of more than one wave train. Where wave crests of one train coincide with crests of another the disturbances are added together, and where crests overlies troughs of equal size they cancel each other. The interference of light may be demonstrated in various ways, in which a single point source must be used in order that the resultant phenomena may remain constant for observation. Two beams from the same source are divided and then brought together again after traversing slightly different paths, either of different lengths or in media of different optical density. In a region where interference occurs, under favourable conditions of observation the illumination is seen to be not uniform, but shows a system of light and dark bands or fringes indicating the reinforcement and annihilation in the overlap of the wave trains. When white light is employed the bands will be coloured owing to the different spacings of those due to the different wave-lengths. If two wave trains interfere, the amplitudes (a) of the displacements added algebraically express the resultant amplitude. With two equal trains out of step by half a wave-length the resultant effect is zero, but where they are in phase the amplitude is doubled and the light intensity ($\propto a^2$) is quadrupled. Thus the energy apparently lost in the dark regions reappears in those which are bright.

The *interferometer* is based on these effects. By measurements of fringe shifts caused by change of optical path of one-half of a divided beam extremely small changes of con-

centration, etc., in gases and solutions can be detected and estimated. The wave-length of monochromatic light is usually found by interference phenomena. Since the measurements are more accurate than those of the velocity of light the 'frequency' is generally expressed as cm.^{-1} ($1/\lambda$) and not as sec.^{-1} (c/λ).

The *colours of thin plates* arise from interference. When white light is incident on thin transparent films, as of oil on water or soap bubbles, the reflected light is coloured. This is because reflections occur from the front and rear surfaces, and for certain wave-lengths the two beams enhance while at others they partially destroy one another owing to their difference of path. Those wave-lengths not reflected are preferentially transmitted. The reflected light shows the spectrum of white light crossed by dark bands corresponding to those wave-lengths removed by interference. The thickness of a film in air can be shown to be given by

$$\frac{n\lambda_1\lambda_2}{2\mu\cos r(\lambda_1-\lambda_2)},$$

where n is the number of dark bands observed in the spectrum between wave-lengths λ_1 and λ_2 , r the angle of refraction of the incident ray in the film, and μ the refractive index. μ is, of course, a function of λ , depending on the dispersive power. If the film is deposited on a surface of greater refractive index, as multilayers of calcium stearate on glass, its refractive index may be found by determining the polarizing angle (i_p), whence $\mu = \tan(i_p)$. The thickness may then be determined by illuminating specimens of known *relative* thickness with monochromatic light at perpendicular incidence. The reflected intensities pass through maxima and minima with the varying thicknesses; minimum intensities being shown at thicknesses equal to $(2n+1)\lambda/4\mu$, where $n = 0, 1, 2$, etc.

Diffraction is another property of wave motion. A train of light waves travelling outwards from a source is not so

simple as that represented in Fig. 1. Imagine the spherical wave front of a wave emanating from a point source. Each 'particle' in the 'medium' of the wave must be regarded as the centre of a new wave spreading out in all directions as soon as the primary disturbance reaches it. Each of these new waves sets up further waves, and so on in a way very complicated to attempt to visualize. The wave disturbances thus spread sideways as well as forwards. The *rectilinear propagation* of light comes about from the interference (with destruction) of all the side waves under ordinary conditions. When obstacles (e.g. opaque disks or holes in opaque sheets) are placed in the light path the complete interference is prevented and some light may be observed passing into the region behind the opaque screen. A point source of light is necessary for observation of the effect. If an opaque strip is placed across the beam, light and dark fringes (coloured if white light is used) are observed outside the region of 'geometrical shadow', while within the 'shadow' the illumination gradually falls off to zero. The sharpness of the shadow edge is thus limited by the *diffraction* of the light, accounted for by the effects of interference of the side-spreading waves above mentioned. The use of transmission or reflection *gratings* for the production of spectra depends on the phenomenon of diffraction.

The formation of *images* by lenses in optical instruments is due to interference effects. At a 'focus' of a lens, rays diverging from a point on an object are caused to converge again, rays which have passed through different zones of the lens crossing at the position of the image. The *image* is thus not a 'point', but a series of interference fringes. These are smaller the greater the angle at which the rays cross and the shorter the wave-length of the light. The sharpness of the image depends on the smallness of the fringe pattern, which limits the *resolving power* of optical instruments. If magnification is carried out beyond the resolving power no further

detail of the object can be brought out in the image. Roughly, the angular measure of two distant points which can be separated by a telescope is equal to the angle a wave-length of light would subtend at a distance equal to the diameter of the object glass. The same limitations on resolution apply to the microscope, and explain the great increase of definition obtained by the use of high aperture objectives. A magnification of $1,000 \times$ (numerical aperture) represents the useful limit attainable with visible light. The *numerical aperture* of an objective is the sine of one-half the angle of the maximum cone of light which it can take from any point on the object multiplied by the refractive index of the medium between object and lens. It may be increased by the use of oil of the same refractive index as glass between the object and the front face of the objective—*oil-immersion objectives*—a device used for high-power microscope work. Particles too small for ordinary microscopic vision may be observed with oblique ‘dark ground’ illumination—the *ultramicroscope*—when they appear as bright specks owing to diffraction of the light round them. The shapes of all small particles, and the structures of any fine detail (e.g. biological detail) of an object, may be so much distorted when translated into images by a microscope that conclusions drawn about them are entirely untrustworthy. Such a state of affairs is betrayed by changes in the appearance of the image under different conditions of illumination.

The definition of an image may be improved by shortening the wave-length of the light used, but the advantage gained by using ultra-violet light is scarcely compensated for by the elaborate and expensive nature of the apparatus necessary. The limit of resolving power using ultra-violet light is about $1,500 \text{ \AA}$, i.e. points nearer than this distance cannot be seen as separate. A great increase in resolution is obtainable, however, by the *electron microscope*. A beam of electrons is employed instead of light, and focused magnetically or

electrostatically. As moving electrons may be treated as a process of wave motion (Chap. III) the action resembles the passage of light through a microscope except that the 'wave-length' is very much smaller. The theoretical resolution is such as to permit of the formation of images of actual molecules or atoms. Resolution beyond about 20 Å, however, is in practice restricted by the difficulties of designing magnetic or electric 'lenses' to function at large apertures; without a high aperture of illumination of course full advantage cannot be taken of the small wave-length.

The above remarks on the resolving power of lenses refer to their power of rendering visible particles of extremely small size. Where images of larger objects are concerned quite different considerations apply. Lenses are subject to a number of imperfections which reduce the definition or sharpness of the image, and this is particularly so when a large lens of short focal length is employed to focus an object of considerable size. These imperfections are intrinsic and quite apart from inaccuracies of manufacture. To satisfy all the conditions necessary for perfect focusing is often impossible, and lenses must be designed for the particular purpose they are required for by balancing the errors to bring them to a minimum. When fields of varying *depths* are viewed through a lens, sharpness of image will be improved by *stopping down*, in contra-distinction from the necessity of using the full aperture of a correctly designed lens for effecting the maximum sharpness of focusing of a small object. In the latter case, if any stop is used, it should cover the centre of the lens and not the outer parts, to secure the maximum 'crossing' of the rays at the image. The 'light-gathering' power of a lens is expressed by the '*f* ratio', the number placed as a denominator to the symbol *f* being the focal length of the lens divided by its diameter or that of any stop used with it.

The passage of light in systems of *oriented particles*—

anisotropic matter—is of importance to chemists. The concept of light as wave motion is based on the observed phenomena of interference and diffraction, and those of *polarization* indicate that the waves are of the transverse type. The property of light of being polarizable is of the greatest use in the optical examination of crystals and other systems of oriented and regularly arranged particles. If the arrangement is one belonging to the *cubic* system, polarization phenomena do not differ from those for isotropic media, but for crystals of lower symmetry the velocity of light varies according to the angle the direction of vibration makes with the crystal axes. This leads to the splitting of the incident light into two rays travelling with different velocities—*double refraction* or *birefringence*. *Tetragonal*, *trigonal*, and *hexagonal* crystals are termed *uniaxial* because along a certain axis—the optic axis—light behaves as if it were traversing a cubic crystal. In other directions there is double refraction. The *ordinary ray* always travels at a fixed velocity (for a fixed λ), that of light along the optic axis, so that the light imagined to spread from one point within the crystal has a spherical wave front. The ray is plane polarized with the electric vector at right angles to the plane of the ray and to the optic axis. The *extraordinary ray*, plane polarized at right angles to the ordinary ray, travels with a velocity varying with direction. Light of this type therefore starting from a point within the crystal spreads as an ellipsoid of revolution instead of as a sphere. As the result of this, the wave front is not at right angles to the direction of the ray itself: there is a certain crab-wise movement of the light, and the relation $\mu = \sin i / \sin r$ does not hold for the ray directions when light enters the crystal. *Positive birefringence* means that the extraordinary ray travels slower than the ordinary ray, and *negative birefringence* the reverse. The difference in velocity between the two rays is most marked in directions at right angles to the optic axis.

Crystals of lower symmetry than the above classes are *biaxial*. Here, in general, entering light rays are split into two extraordinary rays of different velocities, except along two optic axes where the values become the same. These effects arise from the anisotropy of the molecules themselves. The forced vibrations imagined set up by the electric vectors of the light wave (p. 26) are unequal in different spatial directions owing to the non-spherical electric structure of the molecules. If all the molecules were arranged in parallel orientations in the crystal the electrical properties of the molecule could be inferred from the optical properties of the crystal. The application of this is limited by the fact that most crystals are built up of groups of molecules; within the group (of several molecules) the fixed orientations are not those of simple parallelism. When a large positive birefringence is observed it may be inferred that the molecules are either rod-shaped and pointing along one direction, or flat with their planes variously oriented but parallel to a line. A large negative birefringence indicates either flat molecules lying all parallel or rod molecules lying in planes with their lengths not parallel.

The *absorption* of light by crystals may also be strongly anisotropic. It is found, from examples of crystals of known structure (X-ray analysis), that the strongest absorption takes place where the electric vector of the light is correctly related (generally parallel) to the direction of the *chromophoric* groups, e.g. along the lengths of such chemical linkages as —N=N— (azo) which give rise to powerful absorption. If, as is not always the case (see above), molecules of this type are arranged in the crystal in approximately parallel arrays, the crystal will show strong *pleochroism*, i.e. the light absorption will depend on the direction of polarization of incident plane polarized light. Ordinary and extraordinary rays will be absorbed in different amounts. This is markedly shown by crystals of tourmaline, and by 'Polaroid', a film

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containing oriented crystals of an organic tri-iodide derivative. Of incident unpolarized light, only light polarized in one plane is transmitted (with feeble absorption), that polarized in the other being absorbed by the oriented chromophoric groups in the crystals. Similar anisotropic properties are shown when molecules in crystals emit light as *fluorescence*. The emitted light may be strongly polarized and of varying intensity in different directions (p. 169). This is particularly the case in crystals of parallel molecular orientation, as in potassium uranyl sulphate, or in naphthacene in solid solution in anthracene. Here again the polarization and the intensity of the absorption and the emission are related to the orientation of the fluorescent group in the molecule. *Photochemical changes* in crystals may also be anisotropic. Solid *o*-nitrobenzaldehyde, for example, undergoes intramolecular change into *o*-nitroso benzoic acid under the influence of light. The rate of change in these crystals has been found to depend on their orientation when exposed to polarized light. Light with the electric vector in a certain direction relative to the crystals will be most strongly absorbed, and therefore brings about more chemical change; but it is not known whether more feebly absorbed light of different electric vector orientation is less effective when considered on an equal absorption basis.

The optical properties of crystals in polarized light are important aids in chemical investigations. As already mentioned, uniaxial crystals show double refraction except along the direction of the optic axis. A plate of such a crystal cut perpendicular to the axis appears isotropic in *parallel* light. Between crossed Nicols in *convergent* light, however, a characteristic interference pattern is observable, consisting of a black cross and dark rings, with rings of colour if white light is used owing to the variation of refractions with wavelength. Biaxial crystals in convergent light between crossed Nicols, viewed along a direction bisecting the angle between

the two optic axes, show a different but typical pattern. In skew crystal sections the effects are still recognizable, and afford a means of distinguishing the two crystal classes.

The passage of *parallel* light through uniaxial crystal sections in directions not along the axis leads to the formation of ordinary and extraordinary rays following in general different paths. One special case is of great importance.

A plate cut from a uniaxial crystal parallel to the optic axis does not divide into two directions a ray incident normally on it, but the ordinary and extraordinary rays follow the same path at different velocities. If light, plane polarized at 45° with the optic axis, is incident normally on the plate the displacements of the two components of the light resolved along and at right angles to the axis will get in and out of phase as the light reaches different depths in the crystal. When the thickness of the plate is such that one component is retarded by $\frac{1}{4}\lambda$ (i.e. by $\frac{1}{2}\pi$ in phase) over the other, the displacements of the two linearly polarized components combine to produce circular displacements. These can be right- or left-handed. Such a plate, termed a '*quarter-wave plate*', turns linearly polarized light into *circularly polarized* light. Circularly polarized light, passed through a Nicol, resembles ordinary light in that its intensity is unchanged by revolution of the prism. If, however, another quarter-wave plate is interposed, the two linear components are altered a further $\frac{1}{2}\pi$ in phase to π or 0, i.e. they combine to a single plane polarized ray detectable by the Nicol.

The importance of circularly polarized light is that substances with a 'screw-like' structure, as compounds with four different groups tetrahedrally attached to a central atom, or crystal lattices of certain forms (as quartz), transmit right- and left-handed circularly polarized vibrations with different velocities. Since a combination of right- and left-handed

circular vibrations compound into a plane vibration, and difference of velocity means alteration of phase and alteration of the direction of the resultant plane vibration, such bodies rotate the plane of linearly polarized light. Substances showing this behaviour are termed *optically active* and have *dextro* and *laevo* forms of opposite 'screw' structure, rotating the plane to the right and to the left in equal but opposite amounts. The amount of rotation is proportional to the distance travelled by the light, but not exactly to the concentration. The *molecular rotation* of a solution

$$= \frac{\text{rotation (in degrees) per decimetre of solution}}{\text{gram molecules of active solute per cubic centimetre of solution}}$$

This is constant only if the rotation is proportional to the concentration. In strong solutions effects may occur causing serious deviations, e.g. *l*-malic acid rotates the plane of polarized light laevo in weak and dextro in strong solution. The molecular rotation varies with the wave-length of the light employed (*rotatory dispersion*).

Light circularly polarized in opposite directions is not only differently refracted but, if absorption occurs, is *absorbed* in different amounts by a dextro or laevo molecule. Consequently, if it should happen that light absorption decomposes the molecule, a mixture of equal numbers of such molecules exposed to circularly polarized light is unequally affected, so that an excess of one form appears. It is thought that this process, brought about by sunlight circularly polarized by reflection, may be the origin of the characteristic 'optical activity' of molecules of living organisms. If so, all living matter must be imagined as derived from one or a very few chance syntheses from non-living matter, or equal amounts of optical isomers would be found in nature. This is in accord with the very small probability of the spontaneous formation of a very complex molecule.

In the general case of a thin plate of a uniaxial crystal cut parallel to the optic axis, and transmitting light plane polarized at 45° to the axis, *elliptically polarized* light is produced. With a second Nicol prism interference effects are observed. This is because the second prism again splits each component into two, so that four components are produced, having different phase relationships. One pair only is transmitted by the second Nicol, and one of the two components is retarded in phase over the other, while both vibrate in the *same* plane, so that interference is possible. (Interference cannot occur between vibrations at right angles to each other, so that none occurs in elliptically polarized light itself.) If the retardation is 0 or a whole number of wavelengths, light of that colour is extinguished by the action of the crossed Nicols, but the remaining colours of the original white light are transmitted so that the crystal plate appears *bright* and *coloured*. When the optic axis of the plate is turned to coincide with either Nicol axis all light is extinguished. These effects are made use of in the optical examination of crystals and other doubly-refracting media.

In addition to the quarter-wave plate above mentioned, *half-wave* and *full-wave* or *unit retardation* plates have important properties. They are all cut from uniaxial crystals parallel to the optic axis of thickness such that the retardation of one ray over the other is $\frac{1}{4}\lambda$ ($\frac{1}{2}\pi$), $\frac{1}{2}\lambda$ (π), or λ (2π), and when placed in linearly polarized monochromatic light with polarization plane at 45° to the optic axis they transmit respectively circularly polarized light, linearly polarized light with the plane of polarization turned through 90° , and linearly polarized light of unaltered plane. The necessary thickness of the plate depends on the wave-length for which it is to be used. For use in white light a mean λ of about 5,750 Å is chosen. Viewed through a second Nicol, also at 45° to the optic axis, plates for white light show the following interference colours:

<i>Plate</i>	<i>Nicols crossed</i>	<i>Nicols parallel</i>	<i>Thickness of mica required</i> (mm.)
Quarter-wave	Pale grey	Brownish	0.036
Half-wave	Yellowish-white	Indigo	0.072
Full-wave	Reddish-violet	Greenish-yellow	0.144

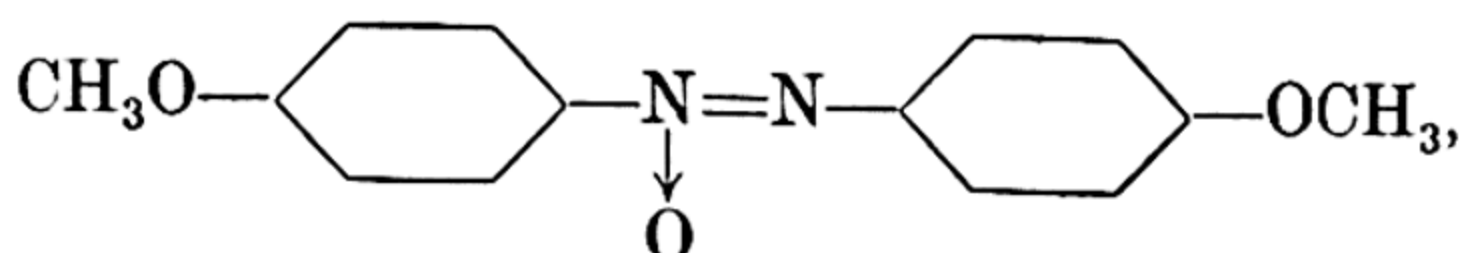
Plates of mica, selenite, or cellophane having the above retardations may be selected by the colour phenomena of the table. The thickness required is given by $\frac{\lambda}{n(\mu_e - \mu_o)}$, where λ is the wave-length, $(\mu_e - \mu_o)$ the 'double refraction' or difference of refractive indices of extraordinary and ordinary rays, and n is 4, 2, or 1 for quarter-, half-, or full-wave plates respectively. Half-wave plates have the property of changing the plane of the electric vector of incident polarized light from one side of its optic axis to the same angle on the other side, and is so used in Laurent's polarimeter. The field is half covered by the plate, and the polarizing Nicol set a few degrees from the extinction position when the analyser is at zero. The electric vector of the light in the two halves of the field then makes equal small angles with the extinction position of the polarizer, so that with the analyser at zero both halves are faintly illuminated. Marked changes in the intensities of the two halves follow any movement of the analyser—the 'half-shade' principle. Monochromatic light of wave-length appropriate to the plate is necessary for accuracy. The unit retardation plate, however, is always used in white light. Set with its axis at 45° to the polarization planes between two crossed Nicols it appears by transmission a violet colour, since the polarized components of the yellow and green light are retarded about one wave-length and are not transmitted by the crossed Nicols. If now a doubly refracting plate of any substance, too thin to show interference colours itself, is interposed in addition the colours extinguished move up or down the spectrum and produce very marked changes of tint owing to the great sensitivity of the

eye to variations in the proportions of red and blue transmitted. The unit-retardation plate is thus used as a very sensitive detector of double refraction.

Thick crystal plates between crossed Nicols merely light up without showing interference colours, unless the optic axis coincides with a Nicol direction, when the field is dark (extinction positions). In thick plates a large number of wave-lengths are retarded to give extinction and others transmitted by the Nicols, resulting in the transmission of a spectrum crossed by many dark bands. The remaining colours blend again to a 'white'. From the number of bands observed with a spectroscope the thickness of the plate can be calculated if its variation of refractive index with wave-length is known. If monochromatic light, plane-polarized at 45° to the optic axis, traverses a plate of doubly-refracting material cut parallel to the axis, and then passes a second Nicol at 90° to the polarizer, the intensity is reduced by the factor $\sin^2 \delta/2$, where δ is the retardation in phase produced by the plate (e.g. π for a half-wave plate).

Flow and stress in materials often brings about double refraction. Models constructed in glass or transparent resins and loaded show the distribution of internal stress gradients by double refraction effects (*photoelasticity*), and this has important engineering applications. Thermal strains in glass-ware are observable in the same way. The effect is recognized by a lighting up of the material when examined between crossed Nicols. A unit retardation plate (above) used in addition increases the sensitivity of the method of detection. A silicate crystal contains a three-dimensional network of oxygen-silicon links regularly arranged, and has the usual optical properties associated with the crystalline state. Glass, while having the same type of internal network of links, does not normally possess the uniformity of internal orientation to behave like a crystal. When stress gradients are present, however, the network is distorted so that light travels at

different velocities in the material depending on the direction of the electric vector. Films of cellophane, produced by rolling out viscose dope, are highly doubly refracting; the molecules having set in the orientations induced by the flow. The optic axis is parallel to the fine lines observable on the surface, the sheet behaving as a uniaxial crystal. Substances with long molecules, as *p*-azoxyanisole,



in the liquid state, show a tendency to orient through the action of van der Waals' forces in groups in the direction of their lengths between particular temperature limits. Even in a liquid such as benzene, where the molecules are small, though very anisotropic, the molecules statistically prefer to form little groups within which they are oriented, and which are constantly breaking up and reforming in different patterns. Substances like the azoxy-compound above, however have a still greater capacity for orientation, so that the liquid is composed of an irregular assemblage of groups internally oriented, each group containing many thousands of molecules and being larger than a wave-length of light. In *smectic* liquids the molecules group themselves in parallel orientations to form flexible sheets one or two molecular lengths thick; in *nematic* liquids long molecules group themselves parallel but retain freedom of movement of sliding past each other. The groups betray their orientation by double refraction effects, and also render the liquid turbid through the light-scattering caused by the abrupt variations of refractive index between the groups.

Liquids are also rendered doubly refracting by the flow gradient when in laminar flow (*streaming birefringence*). The effect is due to orientation induced by the flow, and is shown in its most intense form by colloidal solutions containing rod- or disk-shaped particles. Examples of such rod-like particles

are found in sols of benzopurpurin in dilute aqueous salt solutions, vanadium pentoxide, and certain proteins, while sols of bentonite contain disk-shaped particles. When the flowing liquid is viewed between crossed Nicols along a direction at right angles to the stream lines the dark field lights up if the Nicols are set at 45° to the 'optic axis' developed by the flow. The liquid behaves practically as a plate of uniaxial crystal cut parallel to its optic axis; its refractive index for light whose electric vector vibrates along the optic axis differs from that when the vector is across the axis so that the components of the plane-polarized light passing the first Nicol fall out of step in phase relationship and recombine on leaving the liquid to elliptically polarized light not extinguishable by the second Nicol. Observations may be made when the liquid flows in a tube, but much better, as giving a more defined velocity gradient, is the use of two concentric cylinders, one fixed and one rotating, with the liquid in the annular space, and the light passing parallel to the rotation axis. Here the stream lines in the liquid are circles with centre on the rotation axis. The preferred orientation the particles take up in flow in relation to the stream lines (i.e. the angle between the latter and the developed 'optic axis', 'extinction angle') is experimentally measured by the angle the crossed Nicols must be set to the flow direction at any point in the annular space to pass no light. The crossed Nicols are then turned to 45° from this position to pass the maximum light due to the double refraction, which is then measurable by the use of a Senarmont or Babinet compensator. The 'extinction angle' for very long rod colloids is 0° , i.e. the rods are oriented by flow along the stream lines. On the other hand, freshly prepared sols, with very small particles, and pure liquids, which need much greater flow gradients to show appreciable double refraction, have an extinction angle of 45° . Mathematical theory shows that this is due to the effect of the Brownian rotation of the small particles concerned. No

appreciable fraction of the particles is oriented by the flow along the stream lines. The small rods rotate rapidly and irregularly owing to their thermal energy, and the effect of the flow is to make the rotation somewhat slower when the rods are at an angle θ to the stream lines. In the limiting case of very rapid Brownian movement and consequent very small double refraction effects θ is 45° ; with larger particle size or greater viscosity of the liquid the flow orientation increases and θ takes values nearer 0° . Where the extinction angle is only a little less than 45° it is possible to use theoretical hydrodynamic treatment to evaluate the rotational diffusion constant of the particles and so to estimate their dimensions. Non-uniformity of particle size in real examples often makes the quantitative treatment uncertain.

In the above argument it has been assumed that the rod-like particles are either isotropic to light (but differing in refractive index from their liquid medium) or possess intrinsic double refraction with an 'optic axis' coincident with the rod length. A distinction between these two possibilities may be made by changing the refractive index of the liquid in which the particles are suspended. The double refraction passes through a minimum when the refractive index of the medium is equal to that of the particles. This minimum is zero if the particles are isotropic, while if the particles are themselves intrinsically doubly refracting (i.e. optically anisotropic as well as geometrically anisometric) the minimum is not zero. These effects may be complicated by non-identity of 'optical' and 'geometrical' axes of the particle (as might be shown for example by a rod-like polymer molecule with strongly refracting groups on side-chains), and by penetration of the liquid medium into the particle (as might occur with proteins). Two other complications may be observed. Some particles may be deformable in flow; here the double refraction may increase more rapidly than the flow gradient. Such deformable particles may be micellar

aggregates of polymer molecules and may even be broken down by high-velocity gradients, or may be elastic rods, as the irregularly coiled chains of long polymers, which are subjected to forces of stretching or compression in directions at 45° to the flow lines, behaving in fact like a solid under strain.

Some systems show an interesting connexion between 'streaming' and 'liquid crystal' effects, e.g. solutions of tobacco mosaic virus, the molecules of which are long rods. These orient by van der Waals forces to give a liquid crystal in concentrated solution, while dilute solutions orient only when caused to flow.

An effect caused by orientation in streaming colloidal solutions is also observable in the Tyndall or light-scattering phenomenon. The scattering is greatest when the electric vector of the light is correctly oriented to the line of greatest refractive index of the particles. The scattering of plane-polarized light, passing either along or across the direction of flow, is changed when the anisotropic particles are oriented by streaming, and from the nature of the changes information may be obtained about the 'optical shape' of the molecule. In scattering by colloids depolarization of the light is often observed, so that the scattered light is less polarized than indicated in Fig. 5. Theory shows that such depolarization is due to the optical anisotropy of the particles, and not to their geometrical anisometry in addition. If the particles are anisometric as well, they may be oriented by flow, and this will affect the extent of depolarization of the scattered light, depending on the incident light direction and electric vector orientation in relation to the flow axis and to the direction of observation.

If anisometric colloidal particles are coloured, as in sols of dyes, *streaming dichroism* is observed, i.e. the light absorption varies according as plane-polarized light has its electric vector along or across the orientation axis of the particles. In

this way some information may be derived of the different absorbing properties of polymerized dyes in different directions in the particles. Since the effect is observable only as a difference it is less easily measured than the corresponding double refraction, and occurs only in systems where long rod-like particles can be almost entirely oriented along the lines of flow. Only one Nicol is required, and this should have its vector direction along or across the flow direction, and not at 45° to it, as the crossed Nicols are arranged for double refraction experiments with well-oriented particles.

Photo-dichroism arises when rigid systems of photo-active molecules are exposed to plane-polarized light, e.g. dyes in gelatine films. The molecules appropriately oriented to the plane-polarized light are preferentially bleached or altered in colour; consequently the colour of the system after exposure if viewed in plane-polarized light will vary with the direction of the plane.

Visible light may be polarized by reflection (p. 30), by the use of the dichroic properties of tourmaline or Polaroid, or with a Nicol prism. The latter gives the most perfect polarization, but the size of the prism is limited by the rarity of large crystals of Iceland spar. The prism consists of a crystal of this substance cut across diagonally at a certain angle and cemented together with Canada balsam. The entering light is split into two rays, and the ordinary ray is reflected away sideways at the internal junction while the extraordinary ray is transmitted as plane-polarized light, the electric vector being along the short diagonal of the prism when viewed from one end. Various modified designs have been made, of improved aperture, with end faces at right angles to the beam, or, for economy of calcite, comprising a plate of that material set skew in a rectangular glass prism. Some transmit the ordinary ray and others the extraordinary. For the most perfect extinction it is necessary to use entirely parallel light and prisms with right-angled end faces. For long-wave

ultra-violet light prisms with an air film instead of the balsam are used, but their transmission is poor and aperture small.

When unpolarized light of intensity represented by 2 passes a Nicol prism its intensity is reduced to unity, and after passing a second prism to $\cos^2\theta$, where θ is the angle the second prism is turned beyond the angle of maximum transmission (or to $\sin^2\phi$ if ϕ is the angle from the position of extinction). This result neglects all light losses through imperfect transparency of the prisms.

It is often necessary to analyse the constituents of polarized light. Partially plane-polarized light is detected by the use of a Savart plate or a suitable device of Polaroid and cellophane. The *direction* of the plane of polarization is found by the use of 'half-shade' analysers, as a Cornu analyser or Nicol prism combined with a half-wave plate. The degree of polarization is measured by passing the light through a Wollaston double-image prism, which splits the beam into two diverging components, one with electric vector in one plane (arranged to be the vector direction of the partial polarization) and the other in a plane at right angles. These beams are examined through a Nicol, by the rotation of which they can be brought to equality. If 2θ is the angle between two positions of equality, and I_p and I_s are the intensities of the plane-polarized components of the beam along and at right angles to the vector direction of partial polarization, $\tan^2\theta = I_s/I_p$ (the *depolarization* of the light), whence the *fraction* of the light polarized, $\frac{I_p - I_s}{I_p + I_s}$, may be obtained ($= -\cos 2\theta$).

Elliptically polarized light is analysed by a quarter-wave plate and Nicol prisms, or better by the use of a 'compensator' (Soleil-Babinet or Brace), whereby prisms of quartz or other means are employed to convert the elliptically polarized light into plane-polarized light by introducing further phase

differences between the components. One obtains then the ratio of amplitudes and the direction of the axes of the plane-polarized components of the elliptically polarized light.

When the degree of polarization of light is to be measured, as in the examination of Raman or of fluorescent radiation, or when light intensity is controlled by the use of polarizing devices, care must be taken to avoid errors due to the unwanted introduction of polarization by the passage of light through lenses, plates, etc., in optical instruments.

When light falls on material objects it is *reflected*, *transmitted*, or *absorbed*. When a particular wave-length is chiefly transmitted the body is called transparent to that light. Opaque bodies either reflect or absorb the chief part of the incident light. The differences may be explained by the ways electromagnetic radiations can interact with matter in its various forms. The wave vibrations are conceived as of the nature of alternating electric currents. Matter is treated as built up of electrically charged particles. In these an electromagnetic wave is assumed to generate varying electric movement by 'electromagnetic induction', i.e. the electrical structure of the atom or molecule is distorted. The mathematical theory of wave-motion requires that the induced electric moment shall vibrate at the same frequency as that of the wave, but retarded in phase. The vibrating electric moments of the molecules generate new waves of the same frequency which radiate out in all directions in space. This process is called 'coherent scattering', since the 'scattered' radiation has the same polarization state as the incident radiation and a fixed phase relation to it.

The electrons, atoms, or molecules in matter are bound by forces (electrical attractions) which endow them with 'natural' periods of vibration, like a spring or pendulum. The variation of these periods with the type of process occurring has already been mentioned (p. 5). The nearer the incident radiation frequencies agree with a natural period

of the particle structure the greater will be the amplitudes of the 'forced vibrations' induced; when there is close coincidence the induced vibrations are styled 'free' and become very strong. At this point it is necessary to distinguish carefully between two modes of behaviour of 'natural periods' of matter. Certain natural periods are 'highly damped', that is, when they are excited the energy is converted rapidly into other forms; it may be partly reradiated as fluorescence (which is not of the same frequency as the incident radiation), it may go into chemical energy by dissociating the molecule, or it may become heat energy (through collisions or by internal molecular processes) by being converted into translational, vibrational, or rotational energies. When this happens matter is said to *absorb* the radiation. Processes of *absorption* cannot be dealt with by electromagnetic theory, and are discussed later. It is the 'forced' and 'undamped' vibrations which are of interest here. The electrons surrounding the atom may be conceived of as a 'cloud' of negative electricity. When atoms are traversed by electromagnetic radiation the 'cloud' is caused to vibrate, so that a spherical cloud, for example, becomes effectively drawn out along the line of the electric vector. This vibration lags in phase behind the radiation by an amount determined by the difference between the wave frequency and an undamped natural frequency of the electron cloud of the atom. The 'lifetime' of the vibration so induced is 10^{-14} – 10^{-15} seconds only for visible light unless the frequency is near that of a natural period of the atom, when it rises steeply to 10^{-8} – 10^{-9} seconds. All the energy stored in the atoms by these vibrations is given out again as radiation of unchanged frequency. The induced oscillations generate other waves in all directions which *interfere* with the incoming radiations to produce new waves. The nature of these waves depends on whether the radiation frequency is equal to or different from those of the electrons, atoms, or molecules in the matter. If it is equal, the incident

light is scattered in all directions after traversing a very small amount of matter even in the low-pressure gaseous state. An example of this is when mercury atoms are illuminated by a beam of light of wave-length 2536.52 \AA , a wave-length characteristic of this atom. Even under the low-pressure condition of saturated mercury vapour at ordinary temperature the light cannot penetrate far into the vapour; it is re-radiated in all directions and is called 'resonance radiation', from the 'resonance' between the frequencies. When the vapour is under very high pressure so that the atoms are very close together compared with a wave-length, the light is not scattered, but the waves combine to give *selective reflection*; that is, the surface of the vapour behaves like a reflector, but only for light of exactly the correct wave-length; for others it is transparent. The surfaces of solid dyes often show selective reflection owing to the strong absorption, which is largely 'undamped'. In dilute solution the absorption is weaker and 'damped', i.e. the energy appears as heat and no reflection occurs.

When there is no agreement between the frequency of radiations and of the matter the scattered waves interfere with the incoming waves in a different manner. Let a monochromatic ray of radiation be imagined as incident from a vacuum on to the surface of a transparent material at an angle i (between beam and normal to the surface). As it penetrates the material, secondary waves are generated which interfere with the primary ones to produce complete cancellation in all directions except one (or in the case of doubly refracting crystals, *two*, ordinary and extraordinary ray). This is the ordinary *refracted* ray, having an angle of refraction r between ray and normal to the surface. Theory shows that the refracted ray is in the same plane as the normal and incident ray, and that $\frac{\sin i}{\sin r} = \frac{c}{u}$, where c is the velocity of radiation *in vacuo* and u the velocity of propagation of the

electric vector in the material. The ratio c/u is called the *refractive index* (μ) of the material. Since u varies with the wave-length of the incident radiation, owing to the variations of phase lag of the secondary waves with the difference between the two frequencies of the matter and the radiation, μ is a function of wave-length. It normally increases with shortening of the wave-length, but as the radiation frequency approaches, equals, and then exceeds an undamped characteristic frequency of the matter it passes through a maximum and then a minimum. The wave theory of radiation thus accounts for the observed phenomena of *refraction*, *dispersion*, and *anomalous dispersion* (near a frequency of the matter).

The velocity u above is the *phase velocity* of the final waves resulting from the interference. Under some circumstances (e.g. in metals) it may exceed c . Energy is not carried by the wave, however, at the velocity u but by the *group velocity* v . This comes about from the following considerations. Wave trains are not of infinite length. Unless some singularities ('beginnings' and 'ends') are present the velocity cannot be ascertained. Radiation cannot then be treated as strictly monochromatic; it must be regarded as a collection or group of waves of frequencies varying between $\nu - d\nu$ and $\nu + d\nu$. In a medium of refractive index μ the phase velocity u is c/μ , but the velocity with which energy is transferred, or group velocity v , depends upon the superposition of the above waves of different frequencies, and is given by $\frac{c}{v} = \frac{d(\mu\nu)}{d\nu}$.

The two velocities are equal only when μ is constant, i.e. in a non-dispersive medium, where there is no change of velocity with frequency.

The refractive index of a substance changes in a complicated manner with the frequency of the electromagnetic waves. It has already been pointed out that it undergoes considerable variations in the neighbourhood of an absorption band, but apart from this it varies with the effects produced

on the electrical structure of the matter. At very low frequencies (wireless waves) all the electrical constituents of the matter follow the oscillations of the waves, i.e. electrons vibrate, the atoms in the molecules are displaced so that they vibrate or rotate, and the molecules themselves, if they are electrically dipolar, turn in the periodic field. The electromagnetic theory gives the relation $\mu = \sqrt{\epsilon}$ where ϵ is the dielectric constant; e.g. for water μ for very long waves is about 9, equal to the square root of the dielectric constant. At frequencies round about 10^{15} , i.e. for *visible* or *ultra-violet* light, only the electrons in the outer shells of the atoms can follow the rapidly oscillating field, and μ for water drops to 1.33. The expression

$$\frac{\mu^2 - 1}{\mu^2 + 2} \times \frac{M}{d} = \frac{4\pi}{3} N\gamma,$$

where M is the molecular weight, d the density, approximately gives γ the *polarizability* or *deformability*, and using μ for visible light one therefore obtains the polarizability of the outer (valency) electronic shell of the atoms or molecules, which is a measure of the tightness of their binding. Cations, such as potassium, having a *positive* charge, are, as expected, found to be less polarizable than the corresponding anion (chlorine) having a *negative* charge. Polarizability increases in the series such as F^- , Cl^- , Br^- , I^- owing to the increasing size and weaker forces in the outer electronic shell. Non-spherical molecules are differently polarizable in different directions. By a combination of measurements on the refractive index, the depolarization of scattered light (p. 37), and the Kerr effect (p. 171), the polarizabilities in three directions of space can be evaluated. In this way the polarizability of the benzene molecule is found to be twice as great in the plane of the ring as at right angles to it.

In addition to the phenomena of *dispersion* and *refraction*, *reflection* takes place when radiation is incident at the surface

of matter, while *scattering* and *absorption* are observed in the body of the medium. Reflection is of two kinds, *general* and *selective*. Selective reflection has already been mentioned, and differs from general reflection in being confined to a narrow range of wave-length. General reflection from a transparent surface is a natural consequence of the alteration of the wave velocity, and has a mathematical interpretation in terms of interference of secondary with the primary incident waves. A simple mechanical example is when waves are sent down a long string composed of two sections, one thin and one thick. The retardation produced in the waves when they reach the thick part causes partial reflection of waves back along the thinner section. Only a fraction of the light energy is reflected, depending on the difference of velocity produced at the boundary. From a vacuum (or air) surface of a transparent body, a fraction $(\mu-1)^2/(\mu+1)^2$ of light incident normally is reflected back. This amounts (for the visible region) to about 4 per cent. for glass and to 17.5 per cent. for the diamond.

The fraction of light incident obliquely which is reflected from transparent surfaces depends on its state of polarization. These fractions are given in Fig. 4. The electric vector of unpolarized light may be regarded as having all possible orientations at right angles to the direction of the wave during the time of observation, and the light may be treated by resolving the vectors into two equal polarized vibrations, one parallel and one perpendicular to the plane of incidence. At an angle of incidence where $(i+r) = 90^\circ$ or $\tan i = \mu$, no light is ideally reflected whose electric vectors are parallel to the plane of incidence. Unpolarized light reflected at this angle, the polarizing angle, is practically completely polarized such that the electric vector is perpendicular to the plane of incidence (i.e. is parallel to the surface). The light transmitted obliquely through the surface is partly polarized. A black selenium surface, obtained by melting the element and allow-

ing to cool on a flat plate of glass, is very effective for polarizing light by reflection, especially long-wave light and infrared. Owing to its high refractive index and high value of i as much as 49 per cent. of the incident light is reflected at the polarizing angle of about 70° ; this is practically the ideal limit of 50 per cent.

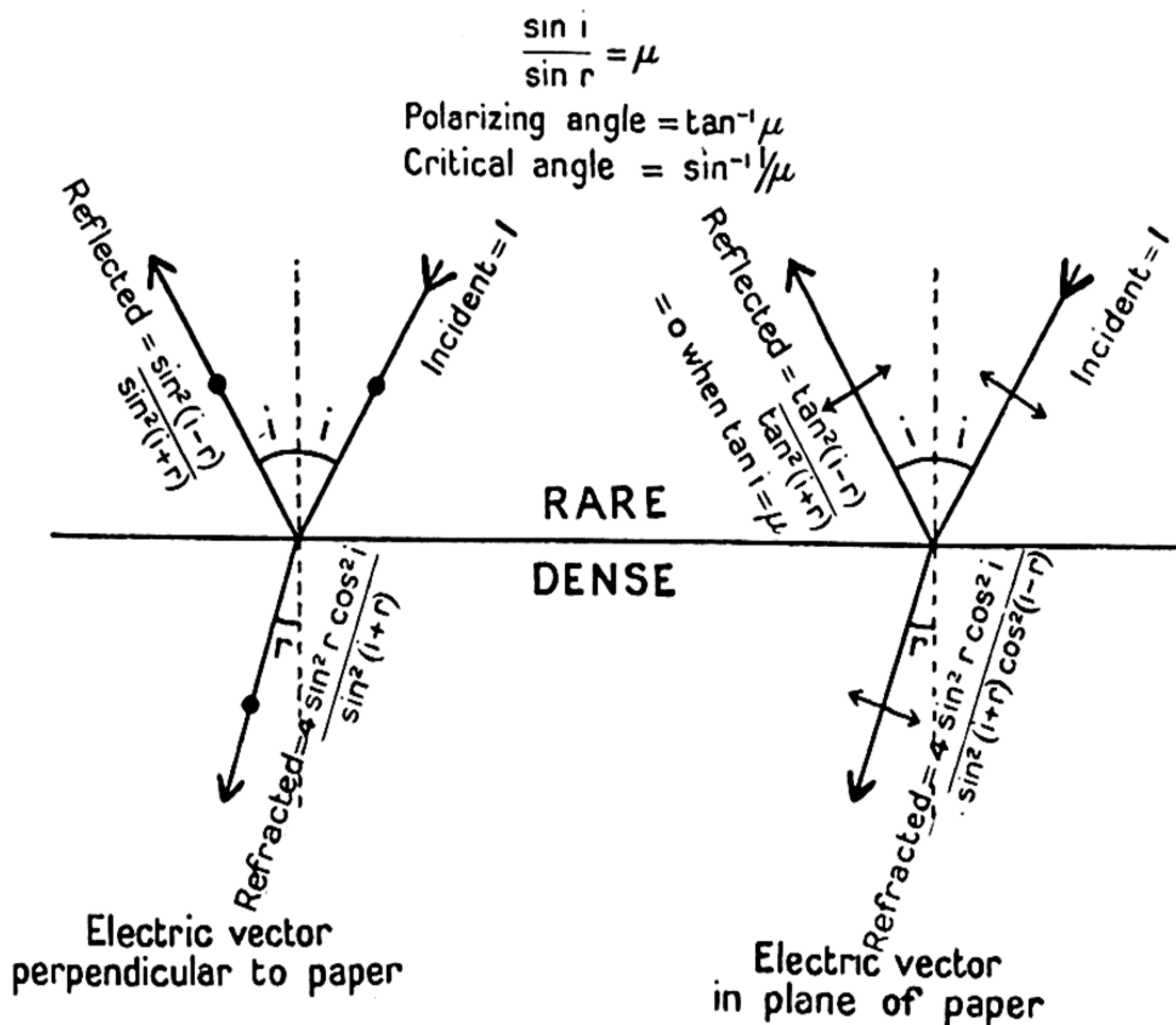


FIG. 4. Reflection and refraction at the surface of a transparent substance.

When the light is incident on a thin transparent plate, two surfaces must be considered, which give multiple reflections. If R represents the fraction of light reflected from one surface, $\frac{2R}{1+R}$ is reflected from a plate and $\frac{1-R}{1+R}$ refracted. The calculation must be made separately for the parallel and perpendicular components of light incident obliquely if it is either unpolarized or polarized at an angle to the plane of incidence. Imperfections of surface and of transparency somewhat alter these values for real plates.

For normal incidence, the fraction transmitted is approximately given by the expression $(1-R)^2e^{-at}$, where t is the thickness of the plate and a the absorption coefficient. Since the latter is a function of wave-length, the relation is only valid for monochromatic light.

The deposition of a thin film of cryolite ($\mu = 1.35$) on glass ($\mu = 1.5-1.65$) effects a notable increase in visible light transmitted from air through the surface, owing to the stepwise reduction in the abruptness of the transition. The same result can be attained by suitable treatment of a glass surface with HF. A boundary having a gradual transition from one transparent medium to another would show no light losses by reflection. By forming a film of such a refractive index on glass that reflections from the front and rear surfaces are equal and of thickness such that interference occurs between them, a non-reflecting glass for normal incidence can be made. This has been achieved by the use of 'built up' multilayers of salts of long chain fatty acids.

If incident at an angle greater than the critical angle $\sin^{-1}(1/\mu)$, light passing through a transparent substance cannot emerge through a boundary with a vacuum or air beyond. It is totally reflected back into the substance. In general a phase change in the light occurs at the surface, different for the parallel and perpendicular components, whereby it becomes elliptically polarized.

The optical behaviour of metals shows peculiar features. They differ from other substances by possessing electrical conductivity. To a first approximation they may be regarded as an assembly of electrons contained within the crystal lattice of positive ions. Two effects of light must be distinguished. Absorption of light may cause electrons to jump to higher energy levels in the metals, and at sufficiently short wave-lengths they may gain enough energy to leave the surface—the *photo-electric effect*. The absorption bands of these processes lie in the infra-red or visible regions for the alkali

metals and in the ultra-violet for others. The mobile electrons in metals lead to other effects. A cloud of free electrons would be completely opaque to radiations since an electromagnetic wave cannot be propagated in matter which has no 'elastic' electrical properties. For longer waves the mobile electrons in the metal will behave as if they were free; for shorter waves the attraction forces in the metal will not permit the electrons to follow the rapid electrical alternations. If the metal is treated as resistanceless, it should be completely opaque for longer wave-lengths and become transparent at shorter. The opacity is not due to *absorption* (free electrons cannot absorb radiation; they can only undergo the Compton effect), but to *scattering* (p. 27), which appears as perfect *reflection* since the electrons are very near together and are set into forced vibrations in phase with each other. We then have the phenomenon of selective reflection not confined to one wave-length but extending over a wide range. Taking the electrical resistance of the metal into account, these ideal results become imperfect reflection at longer wave-lengths and incomplete transparency at the shorter. Thin films of the alkali metals are transparent in the ultra-violet region. Silver films have a transmission band (and feeble reflection) at about 3,000 Å separating the long-wave 'conduction electron' opacity from a shorter-wave region of absorption due to change of energy levels.

Phase changes in the light occur on reflection from the surfaces of metals. At normal incidence the phase changes by π and the reflected waves form a system of standing waves with those incident, while at grazing incidence there is no phase change. At other angles of incidence the phase change is different for the parallel and perpendicular components of the light, so that elliptical polarization results. This effect may be treated by the electromagnetic theory to give information about the optical constants of the metals. The reflective power of metal films falls off when the thickness

is less than 500 Å; a fact of importance in the construction of lightly silvered plates for optical instruments.

It has already been mentioned that a ray of monochromatic light entering a transparent medium induces electrical vibrations in the matter which themselves generate new waves, travelling in all directions, these interfering with the primary waves with destruction in all directions except one—that of the *refracted* ray. If the medium, however, is not *optically homogeneous*, the destruction of the secondary waves is not complete, and a certain amount of the scattered light is observable in other directions than that of the refracted ray. The effect is most marked in turbid media, i.e. media containing small particles of size somewhat smaller than a wave-length of the light. Molecules and atoms, however, though much smaller than light waves, may be regarded as offering to the light waves fluctuating regions of different optical density, and very faint scattering from them is observable. The Rayleigh scattering, as the phenomenon is called, is thus determined by variations of refractive index within the media and is subject to the same considerations as those used to explain dispersion. The problem is treated as one of ‘forced electrical vibrations’ set up by the light in the ‘particles’. Each particle takes up a light vibration (having a certain electric vector orientation) and emits it again with the orientation unchanged. The emitted light has a circular distribution round the electric vector direction.

In a theoretical analysis of the problem Lord Rayleigh showed that the total scattering in a direction making an angle θ with that of the light from a transparent sphere of radius r and small compared with a wave-length (less than 500 Å diameter) is proportional to

$$\frac{r^6(1 + \cos^2\theta)}{\lambda^4}.$$

It is also dependent on the refractive indices of the particle

and the medium. The inverse fourth power of the wavelength relation explains the use of filters passing only red and infra-red light as a means of obtaining long-distance photographs under misty conditions, and also the blue of the sky. Since light displacements are always transverse, no light is scattered in a direction at right angles to the direction of the incident light and parallel to its electric vector. The

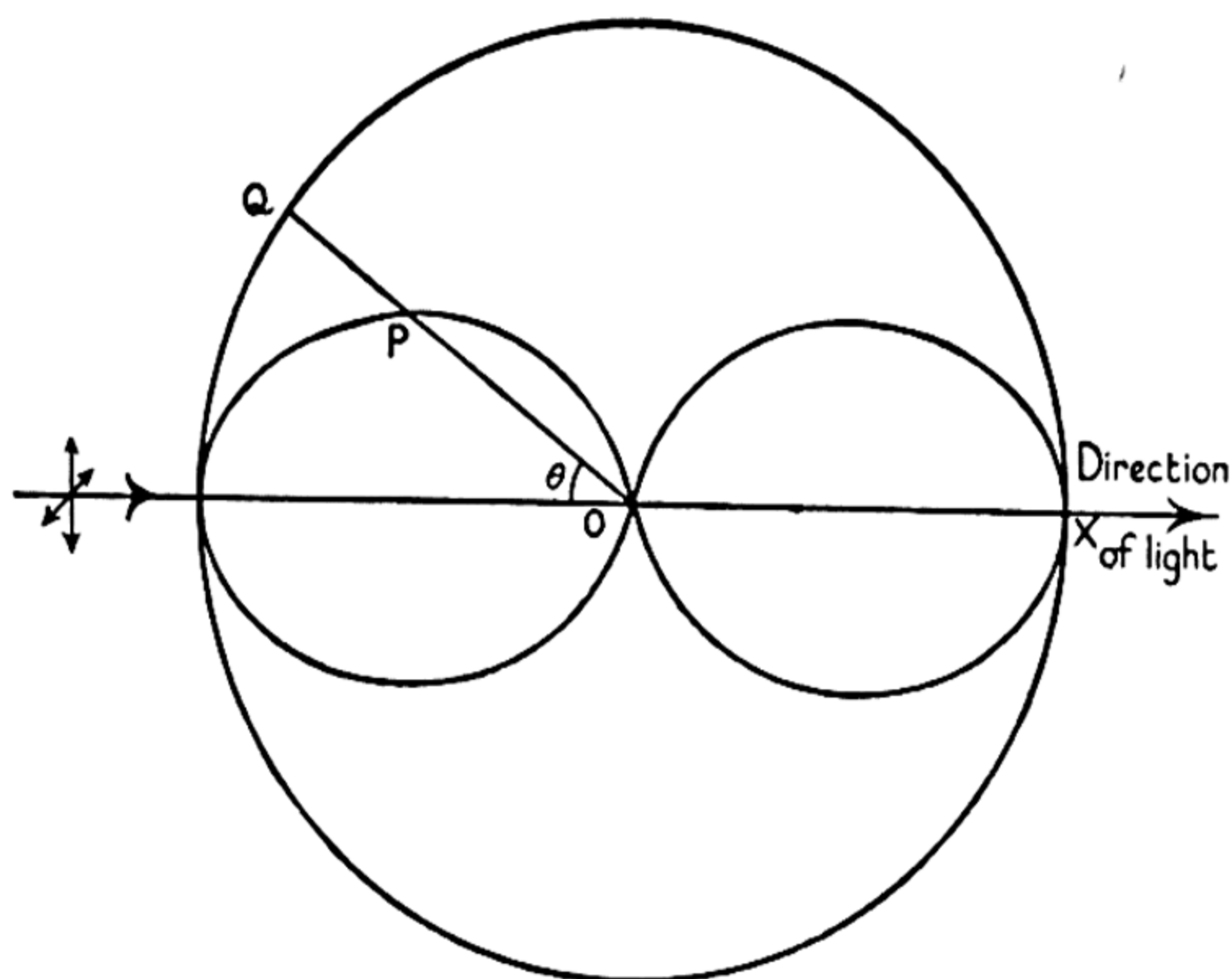


FIG. 5

scattered light distribution is given by the inner curve of Fig. 5 ($r = \cos^2\theta$ in polar coordinates), if the electric vector is in the plane of the paper. The scattering particle is located at O , and any radius OP is proportional to the amount of scattering at the angle θ . Light in this direction is polarized with its electric vector in the plane of the paper and perpendicular to OP . The spatial distribution of the scattered light is given by the surface formed by the rotation of the curve about a vertical axis (i.e. about the direction of the electric vector of the incident light). Radii, as OQ , of the outer circle represent the intensities of light scattered, if the original electric vector had been at right angles to the plane of the paper. For unpolarized light the total scattered intensity along OPQ is $OP + OQ$ ($\propto 1 + \cos^2\theta$), the separate

values giving the intensities of the components of the polarized scattered light, and its spatial distribution may be obtained by rotating the curve given by the sums of these radii about the light direction. The degree of polarization along OPQ is given by $(OQ - OP)/(OQ + OP)$. If the scattering is feeble, the light distribution round a small spherical volume element will be identical with that shown in the figure for a single particle in the system.

The above treatment represents a very idealized system, and depends on the assumptions of *spherical homogeneous* particles small compared with the light wave-length. Real examples of scattering are more complex. Scattering by pure fluids is very small but detectable. As it obeys the λ^{-4} law it appears blue when white light is used. It arises from local fluctuations in density due to random thermal motion, and since these fluctuations are not perfectly spherical, the scattered light is imperfectly polarized (see below). As the particle size in a given scattering system is increased from molecular dimensions up to about 500 Å, the amount of scattering from an assemblage of particles increases proportionally to $r^3\lambda^{-4}$, if comparison is made on the basis of equal weights of scattering material per unit volume, and the solutions are sufficiently dilute to prevent multiple scattering. With large transparent particles (e.g. ground glass) the light is scattered by internal reflections, and the amount of scattering on the same basis as above becomes proportional to r^{-1} , i.e. *decreasing* as the particle size increases, and being no longer dependent on the wave-length, so that white light is scattered as white. In the colloidal range of particle sizes $r = 500\text{--}2,000$ Å light scattering is called the 'Tyndall effect' and is due to diffraction phenomena of great complexity, so that the variation with r and λ cannot be accurately estimated theoretically. At a particle size of $r \approx \lambda/4$ ($\approx 1,000$ Å), i.e. for many colloids, smokes, etc., the amount of scattering rises to a maximum. For very small particles, each particle scatters

only a minute fraction of the light, and scatters it in all directions except that of the incident electric vector. Larger particles scatter mostly in a forward direction at angles not far from the direction of the incident beam. At a radius of about 800 Å for opaque particles the 'shadow effect' becomes greater than the true scattering, light then being chiefly scattered sideways. Over an intermediate particle size range the colour of the scattered light may pass from blue through green and red to white with increase in r . These considerations emphasize the need for close control of experimental conditions to ensure reproducibility of particle size when estimates of concentrations of substances by light scattering are carried out. Matters are simpler when all the particles are larger than 2μ (i.e. when they settle in ordinary liquid systems by Stokes's law in a period of minutes or hours). Here the light scattering is proportional to the projected areas of opaque particles, if the solution is sufficiently dilute to prevent multiple scattering (< 1 gm./litre for 1–2 cm. thickness of observed layer). For extremely dilute solutions light scattering for chemical purposes is best observed at right angles to the incident beam (nephelometry), but for stronger solutions or those containing opaque particles the 'turbidity' or light reduction by transmission is more accurate. Recent developments in the theory of scattering enable measurements of the dependence of scattering power and of refractive index upon concentration to be used as a means of obtaining weight-average molecular weights of the large molecules of certain plastics in solution.

Under certain conditions it is possible to gain information about the shapes of particles, whether roughly spherical or non-spherical, from the polarization of their light scattering, but the quantitative side of the subject bristles with difficulties. In a rough way it is possible to see how anisotropic particles give less polarization in their scattering than spherical particles, since the electrical effects induced in

them, and which determine the vector direction of the scattered light, lie along directions which are a compromise between the original vector direction of the light and the direction of greatest polarizability of the particle. The scattered light vectors are therefore not parallel but grouped in a large solid angle (see p. 40).

If high concentrations of transparent large particles are

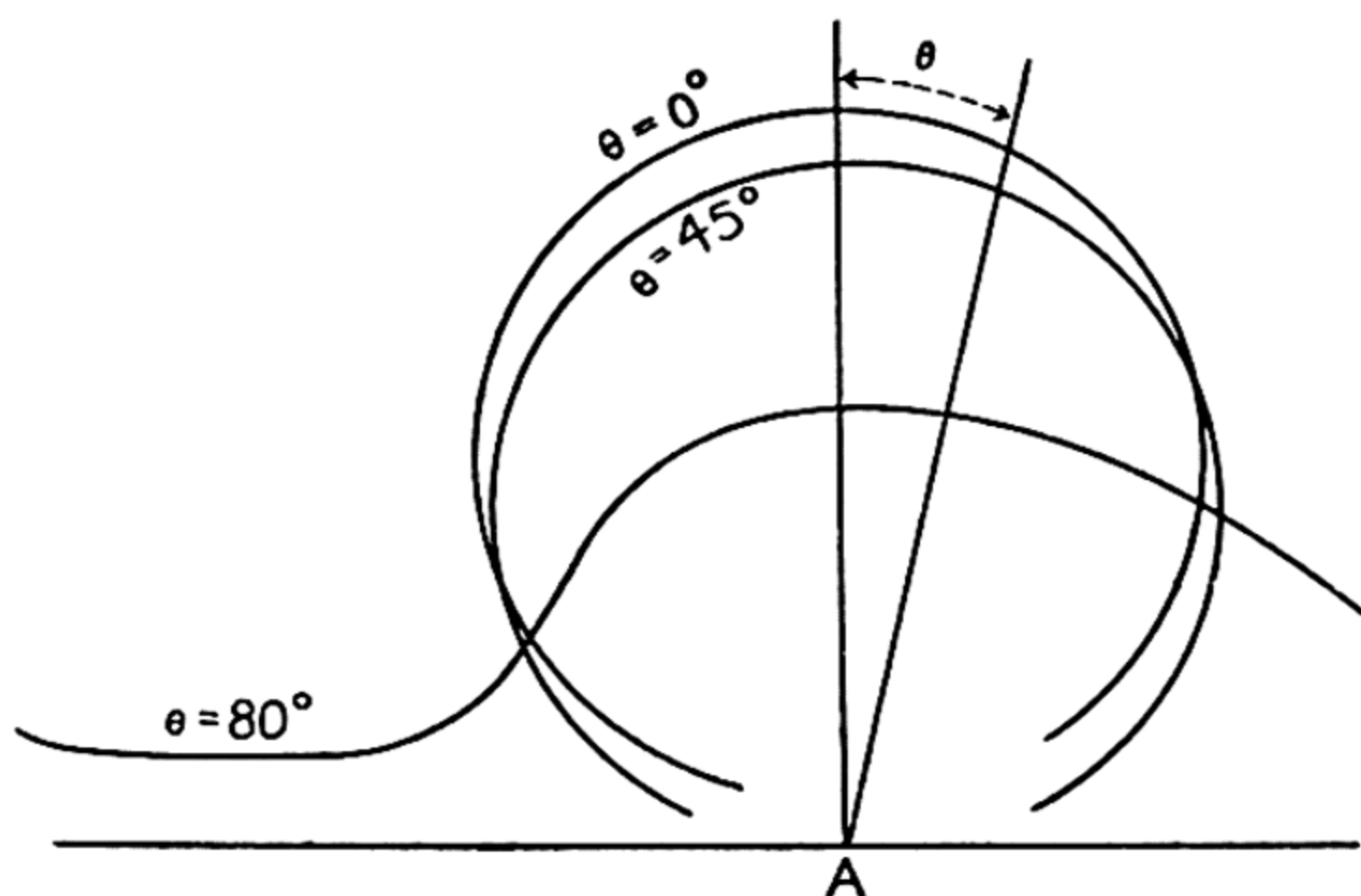


FIG. 6

used, multiple reflections throw more light backwards than forward, and scattering passes into *diffusion*, as observed with milk or paper. The light distribution from a point on an ideal diffusing surface is represented in polar coordinates by a sphere tangential to the surface at that point. This is independent of the angle of incidence of the light falling on the surface. The length of any chord from the point to the surface of the sphere is proportional to the intensity of diffusion in that direction. Substances approximating most closely to this behaviour are magnesium carbonate and magnesium oxide. The former diffusively reflects 90 per cent. at 2,500 Å and 97 per cent. in the visible region. Fig. 6 shows the polar diffusion curves for magnesium oxide at different angles of incidence. They approximate to the ideal shape at incident angles of 0° and 45°, but at much larger angles they are distorted towards the other extreme case of specular reflection

COLOUR PHENOMENA

I. ABSORPTION

A TRANSMISSION



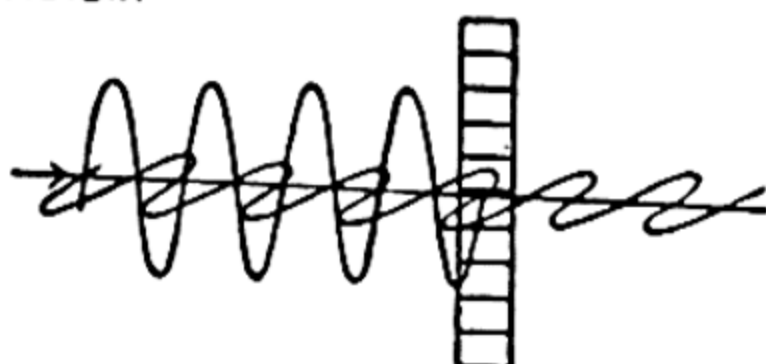
Light vibration taken up by molecule and 'damped', i.e. molecule passes to 'excited state' and loses its energy ultimately by conversion into heat or chemical change. Examples: permanganates, indigo, and the majority of coloured substances.

B PIGMENTS



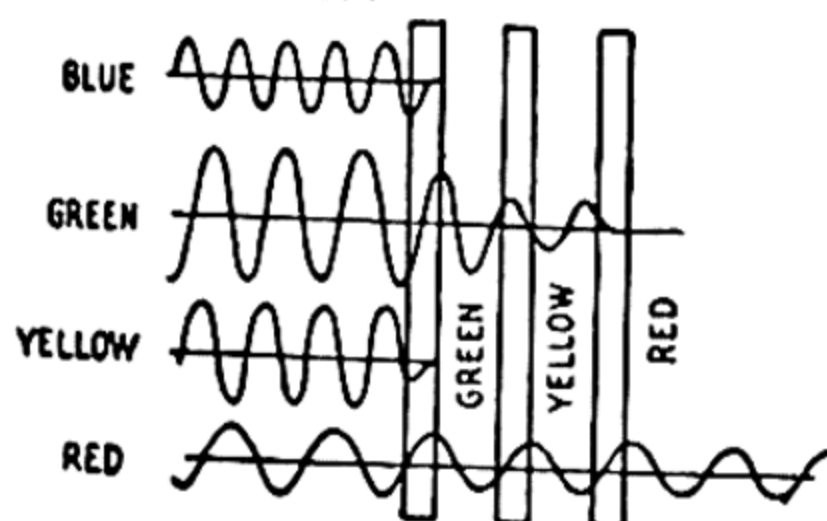
Greater depth of colour with greater particle size. Examples: crushed coloured glass, mercuric oxide.

C DICHROISM



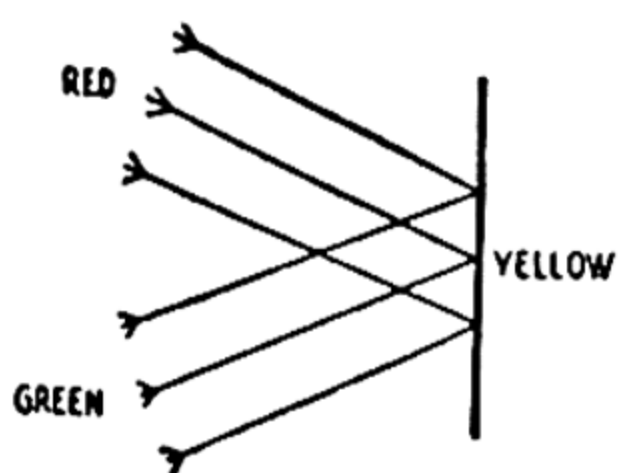
If molecules have a directed chromophoric group and are all arranged almost parallel in the crystal, plane-polarized light vibrating one way is absorbed and the other way transmitted. Examples: tourmaline, azobenzene, polaroid.

D DICHROMATISM



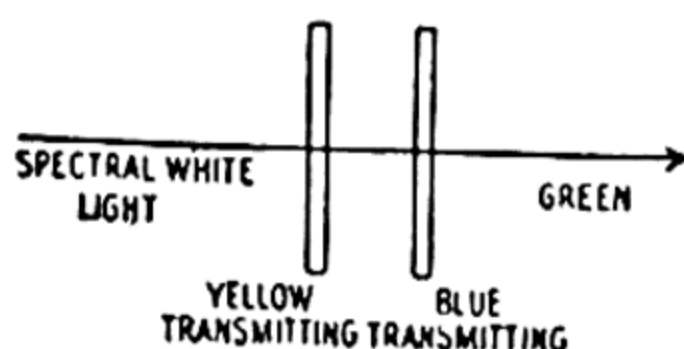
Variation of transmitted colour with thickness and with quality of illumination. Example: mixture of alkaline litmus and chromate solutions; solution of methylene green. Most dyes are red in concentrated solution, changing to their characteristic colours on dilution, e.g. magenta, malachite green, bismark brown. The effect is sometimes inaccurately called dichroism. If its presence is not recognized, difficulties may be encountered in colour tests on thin objects in microscopic work.

E MIXED COLOURS; ADDITIVE



Example: Lumière or Paget Colour Screen.

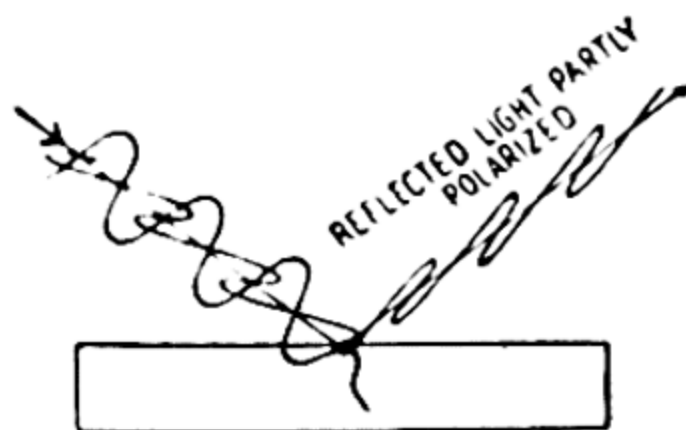
F MIXED COLOURS; SUBTRACTIVE



Green light transmitted if yellow and blue have wide overlapping transmission bands. Example: mixtures of yellow and blue paints.

FIG. 7

2. SELECTIVE REFLECTION



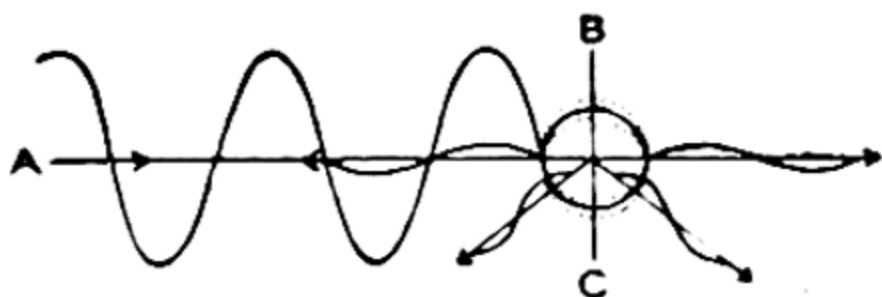
If frequencies of incident light are different from any characteristic frequency of the matter a small amount of the light is reflected, the remainder being refracted, e.g. glass surfaces. (See Fig. 4.)

If frequencies of incident light practically equal a characteristic frequency, we have either (a) normal absorption (see 1 above), occurring in layers of some depth, or (b) selective reflection, when extinction coefficients are extremely high and the wave does not penetrate the surface for more than a fraction of a wave-length. The reflecting power depends both on the refractive index and on the extinction coefficient. Under these conditions of selective reflection the refractive index passes

through a maximum and then a minimum over a narrow range of increasing frequencies bracketing the characteristic frequency of the matter (anomalous dispersion). The light most powerfully reflected will therefore lie on the long-wave side of the true absorption band and there will be a defect of reflectivity on the short-wave side owing to this refractive index effect. Examples: surface colour of solid magenta, methyl violet, magnesium platinocyanide, dimethylnaphtheturhodine. The frequencies reflected are therefore not the true replica of the frequencies most strongly absorbed, and they vary with the relative refractive index of the surface, e.g. dyes deposited from alcohol on glass.

3. SCATTERING

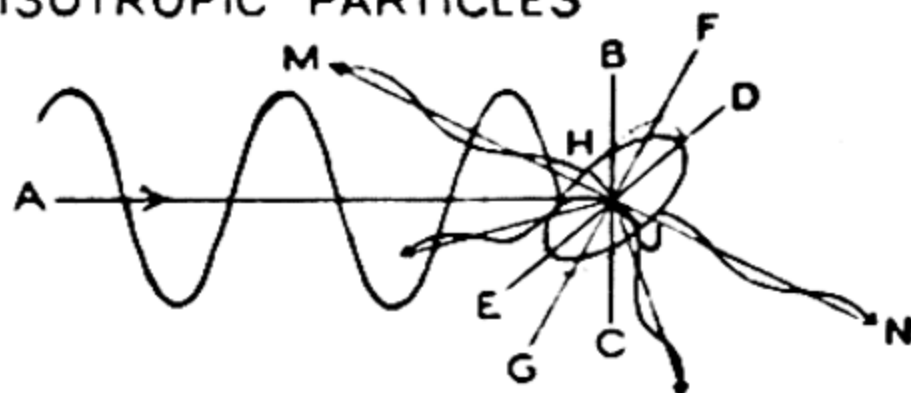
A SPHERICAL PARTICLES



Particles small compared with a wave-length λ . Fraction of light scattered varies as λ^{-4} , hence red light preferentially transmitted, blue light most scattered.

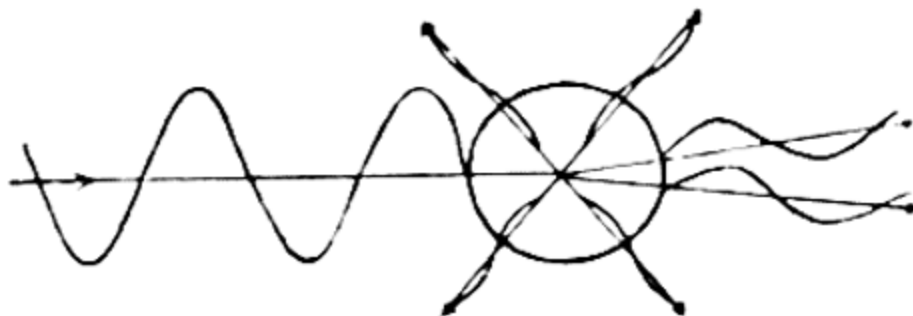
Homogeneous and electrically insulating spherical particles. Valency electrons in particle set into forced vibrations slightly out of phase with incident waves. Resultant of this vibration and primary radiation gives scattered waves. If incident light is polarized with electric vector in plane ABC (plane of paper), scattered light is emitted in all directions round the axis BC ; no light is scattered along direction BC . Examples: blue of the sky, colour of setting sun and street lamps in fog.

B ANISOTROPIC PARTICLES



Anisotropic particles. Incident light polarized with vector in plane ABC . Optic axis of particle DE . Primary light vibrations along BC distort electrons along resultant FG , since polarizability is greater along DE than along HJ (short axis). Scattered light is emitted along the radii of the disk with MN as diameter, polarized with vector perpendicular to disk. With many particles of different orientations the result is less perfect polarization of the scattered light than in case A, together with scattering along BC . This effect depends on actual differences of refractive index along the directions DE and HJ and not on mere anisometry of isotropic particles. Examples: bentonite suspensions.

4. DIFFRACTION

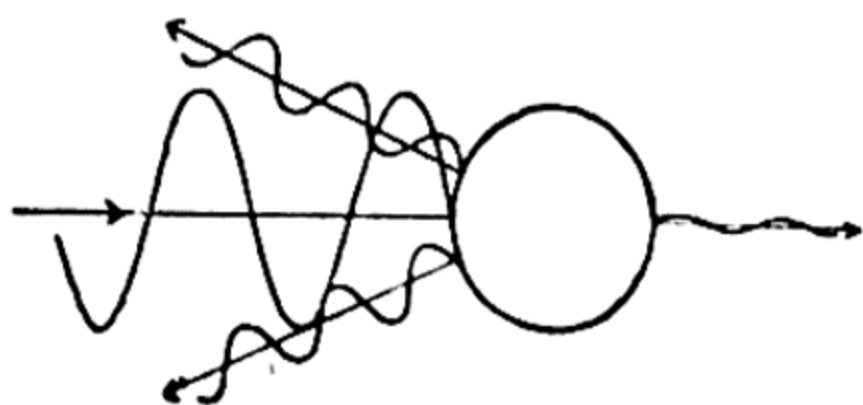


Particle of radius $\sim \lambda/4$. Most of the light thrown forward. Intensity distribution and polarization depend in a very complex way on particle size, shape, and refractive index. The diffraction varies steeply with wave-length for certain particle sizes of substances with high refractive indices; hence white light when diffracted is

coloured. Diffraction effects are strong only when the refractive index of the particles is large. Examples: sulphur sols, oxide layers on metals (diffracted light reflected from metal surface). 'Abnormal' polarization effects sometimes found. Example: fog made by heating nitrosodimethylaniline.

FIG. 7 (cont.)

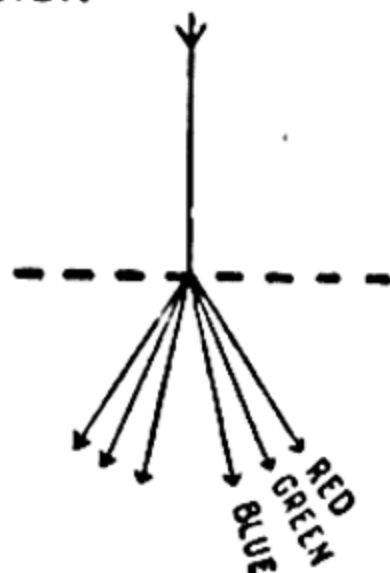
5. OPTICAL RESONANCE



When very small electrically conducting particles intercept light waves, their conduction electrons oscillate, and for each particle size there will be a particular frequency for which there is resonance between the waves and the 'electric circuit' within the particle. At such a coincidence there will be strong reflection or scattering, while other wave-lengths will pass by. Examples: coloured silver sols, ruby glass containing gold, thin films of the alkali metals condensed on glass.

6. GRATINGS

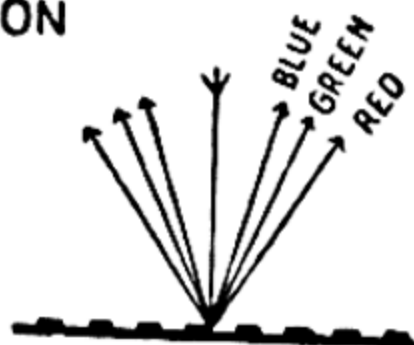
A TRANSMISSION



Wave-length λ diffracted at any angle is given by:

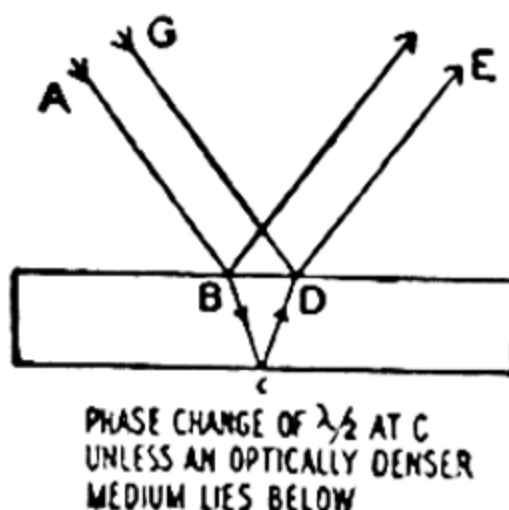
$n\lambda = (a + b)(\sin i + \sin d)$ where n is any integer, a = width of clear space, b = width of opaque space, i = angle of incidence, and d = angle of diffraction. For any angle at which the grating is viewed (across the rulings) monochromatic light will be seen, since along any one direction diffracted wavelets spreading outwards from each grating space will all be in phase for one wave-length only.

B REFLECTION



This type of grating shows a colour sequence with changing angle of incidence opposite from a grating of parallel plates (7, below). Example: structure colours of feathers and insects.

7. THIN PLATES



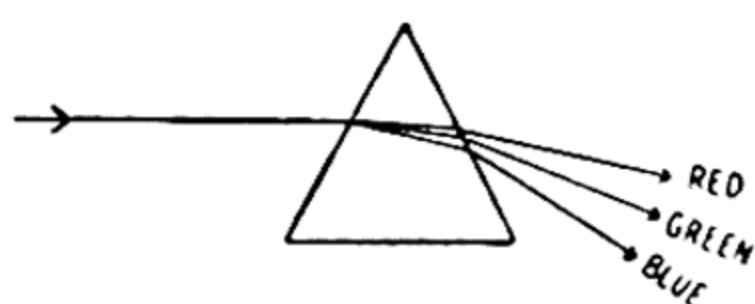
A ray GDE reflected from the upper surface of a transparent medium will interfere destructively with a ray $ABCDE$ reflected from the lower surface, if the path difference between the rays is λ , 2λ , etc. (since a phase-change of $\lambda/2$ occurs at the lower reflection). This wave-length will therefore be cut out of white light. If the lower surface is in contact with a still denser optical medium, interference occurs for values of path differences of $\lambda/2$, $3\lambda/2$, etc. White light reflected from a film shows the complete spectrum crossed by narrow dark bands, few or many depending on the thickness of the film. The colours are therefore very unsaturated. Examples: soap bubbles, oil films on water, pearls. The effects are intensified and the reflected light made

increasingly monochromatic (widening of absorption band and narrowing of reflected band) where many reflecting planes are superimposed. Examples: fiery opals, certain $KClO_3$ crystals. The reflected light bands move towards shorter wave-lengths with increasing angles of incidence.

Coloured films may be observed on *metal* surfaces even though thinner than a wave-length, e.g. oxides or condensed vapours. This must be ascribed to differences of phase-changes in the waves on reflection from the two surfaces, and not to interference by path difference. The problem is difficult theoretically since for such thin films the two reflections cannot be treated as two independent processes.

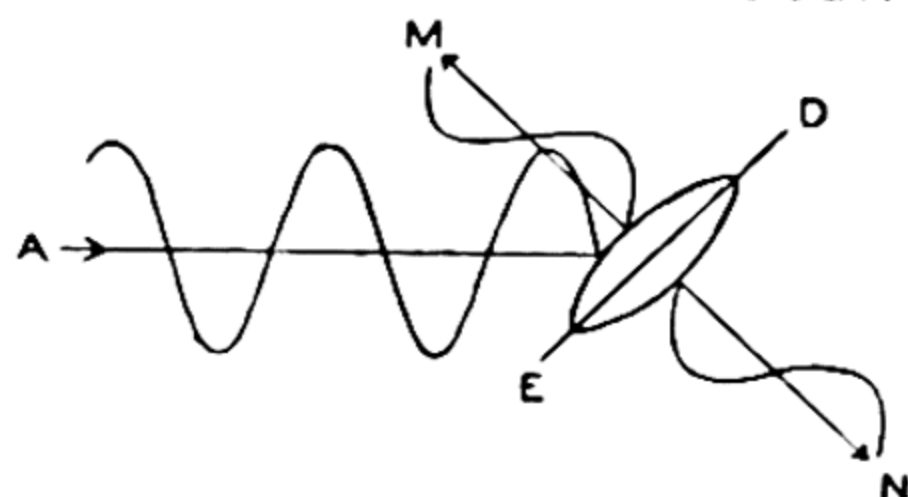
FIG. 7 (cont.)

8. DISPERSION



Example: glass powder and a liquid mixture of the same refractive index for one wave-length but of different dispersion; chromatic emulsions of nitrocellulose.

9. FLUORESCENCE



Molecule with a chromophore along DE absorbs a part of the incident light from A given by resolving the intensity along DE . The excited molecule re-emits after a time interval, during which the molecule may or may not have rotated away from its original orientation. Fluorescence emission is round a disk with MN as a diameter, perpendicular to DE , and polarized with electric vector parallel to DE . With molecules in all orientations and no rotation the maximum degree of polarization of the fluorescent light when observed along a direction perpendicular to the direction of the incident light and to the plane of the paper is 0.5.

10. COLOURS OF THIN PLATES BETWEEN CROSSED POLARIZERS

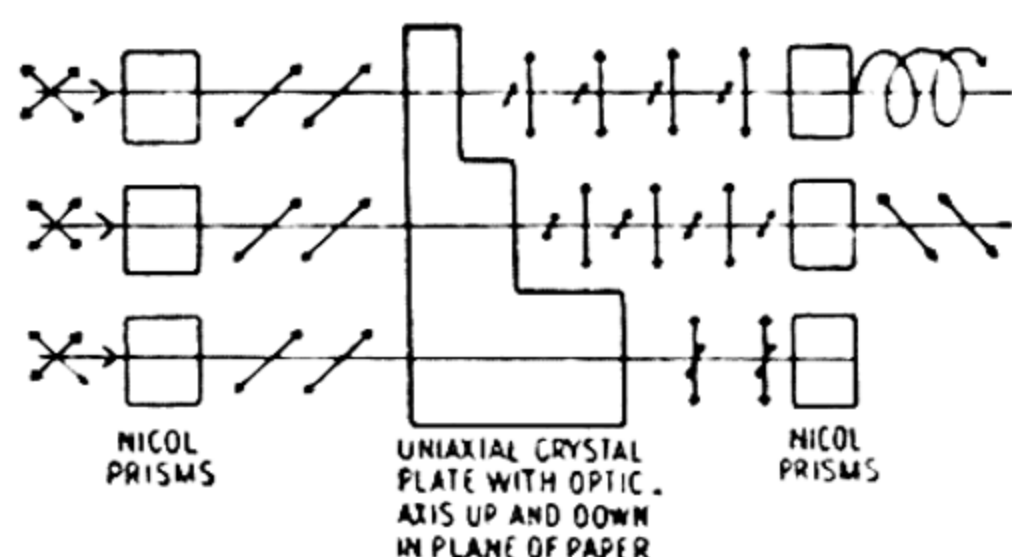


Diagram shows three thicknesses of a plate of a uniaxial cut parallel to its optic axis. Plane-polarized light vibrating in a plane at 45° to the plane of the paper enters the crystal. The vibrations are here divided into two resolved parts, one along and the other across the optic axis, which travel at different speeds and therefore get out of step. The first thickness shows quarter-wave retardation of one wave over the other, from which a second polarizer in a crossed position to the first yields circularly polarized light. The second thickness shows half-wave retardation for light of one wave-length. This is passed by the second polarizer, but light of other colours is partly cut off. The last thickness shows retardation of one wave; if this is in the middle of the visible spectrum, this light is cut out by the second polarizer, and only the red and blue ends of the spectrum transmitted.

FIG. 7 (cont.)

(cf. the curve for 80°), i.e. the surface begins to show *surface gloss* instead of being *matt*. If the particle size lies between certain magnitudes there will be a change-over from diffusion to specular reflection as the wave-length of the radiation is increased (e.g. a surface matt to visible light may reflect infra-red rays) or as the angle of incidence is increased.

The ideal law of distribution of diffused light round a surface applies also to the brightness of an element of a self-

luminous surface, emitting light by temperature radiation. The equation giving the polar curve of Fig. 6 is $I_\theta = I_0 \cos \theta$, where θ is the angle between the direction of observation and the normal to the surface, and I_θ and I_0 are the intensities at angles θ° and 0° . A whole surface emitting or diffusing light has a brightness (p. 45) independent of the angle θ at which it is viewed, as the reduction due to the $\cos \theta$ term is exactly compensated for by the larger number of emitting elements subtended by the eye at oblique observation. This law does not hold for reflecting surfaces, nor where polarization effects occur in luminescence phenomena.

The colour of *pigments* (when it does not arise from the comparatively rare effect of selective reflection) is due to the removal from white light by absorption of certain colours with diffusion of the remainder. The finer the particle size, the shorter the light paths before back diffusion occurs, and so the less the absorption. Fine grinding of pigments, especially those of low absorption power, will therefore diminish their depth of colour, as red glass may be crushed to a white powder. If the pigment has a high enough absorptive power to remain coloured when its particles are reduced to a size comparable with a wave-length of light, scattering effects from the small particles combining with the true colour may produce marked changes of tint.

To fix the relative scale of matter and radiation more clearly in the mind the familiar device of magnification is useful. If increased in size three-millionfold, $1,000 \text{ \AA}$ becomes one foot, and atoms would be as large as the full-stops on this page, while molecules would be as large as one of the printed characters. Colloidal particles would range from the dimensions of a word to about 2 feet; the upper limit representing the particle size above which suspensions appear turbid. Smoke particles might be a yard in diameter. The optical microscope would distinguish particles between 2 miles and 1 yard across, and the ultra-microscope down to a third of an

inch in favourable cases, i.e. metal sols. The electron microscope, working on our new scale of sizes between 20 yards and one-third of an inch, has the advantage over the latter instrument in rendering particle shapes visible. On this scale red, green, and blue light respectively would have wave-lengths of 7, 5, and 4 feet, and ultra-violet light 4–2 feet. The wave-length of infra-red radiation corresponding to molecular vibrations would be about 25 yards and that of molecular rotations about 250 yards. The whole of this range of electromagnetic radiation has a much greater linear extension than the matter which produces it.

Fig. 7 diagrammatically illustrates the different ways in which colour effects of interest to the chemist may arise.

II

LIGHT AND LIGHT SOURCES

FOR the measurement of *illumination*, light is evaluated in terms of its capacity to produce visual sensation. The unit of *intensity* of light sources is the International Candle Power, defined in terms of the emission of certain electric lamps preserved as standards. The Hefner Candle, a continental European unit, = 0.9 I.C.P. The unit of *luminous flux* is the Lumen, and is equivalent to the flow of light in unit solid angle from a uniform point source of 1 C.P. The total flux from a source of 1 C.P. is therefore 4π lumens, and for a non-uniform source (emitting light flux varying with direction) we have Spherical Candle Power = Total lumens emitted/ 4π . The unit of *illumination*, i.e. of the density of luminous flux *received* on a surface, is the Lux or Metre Candle, and is equal to the illumination received by a surface, normal to the light direction, from a point source of 1 C.P. 1 metre away. Another unit, the Foot Candle, = 10.764 lux.

The *brightness* of a surface, whether acting as a primary emitter or as a reflector (diffuser), is measured in Lamberts. One lambert corresponds to the emission of 1 lumen from 1 sq. cm. of the surface. Objects in sunlight have a brightness of the order of 1 lambert; indoor brightness may be 1–10 milli-lamberts. Brightness may also be expressed in other units. The 'equivalent foot candle' is the brightness produced by the illumination of 1 foot candle on a perfectly diffusing surface reflecting 100 per cent. of the incident light. For such surfaces 1 equivalent foot candle = 1 foot lambert = 1.076 milli-lambert = 0.318 candles/sq. foot. As the wave-length sensitivity of the eye changes its form between 1 and 10^{-4} equivalent foot candles (most rapidly between 0.2 and 0.001; see Chap. IX, Purkinje effect), the comparison of brightnesses of different lights within these

limits (e.g. phosphorescent substances) must be made with due regard to the differences of wave-length distribution of the sources to be compared.

At the wave-length of maximum photopic eye sensitivity, 5,560 Å (reckoned on an energy basis), 670 lumens equal 1 watt. The theoretical limit for 'white' light is 110 lumens per watt. No light sources are so efficient as to produce this light flux per watt of power consumed. The ordinary tungsten filament lamp produces 12–15 lumens per watt, and newer high-pressure types of mercury arcs may give about 50.

Many light sources are based on the temperature emission of hot bodies. An ideal 'total radiator' (black body), capable of absorbing all radiant energy which falls on it (experimentally approximated to by an enclosed space with a small hole for radiation to emerge), emits radiation according to certain laws. The hemispherical radiation given out by such a body may be calculated from the equations:

Total radiation

$$= 5.67 \times 10^{-5} T^4 \text{ ergs per second per sq. cm. (Stefan's law).}$$

Intensity of radiation at wave-length λ (measured in cm.)

$$\begin{aligned} &= I_{\lambda} d\lambda \\ &= \frac{3.703 \times 10^{-5} \lambda^{-5} d\lambda}{(e^{1.438/\lambda T} - 1)}. \quad (\text{Planck's law.}) \end{aligned}$$

These expressions refer to radiation into space at the absolute zero. For surroundings at other temperatures it must be remembered that a radiating body receives as much energy from its surroundings of temperature T as it would emit into space at the absolute zero if it were at the temperature T , and this quantity must be deducted in estimating its emission.

For each value of T in the relation above there is a value of I which is a maximum, proportional to T^5 , at a wave-length λ_{max} (cm.) given by $0.2885/T$. Curves of intensity

distribution are shown in Fig. 8. It will be seen that very high temperatures ($\approx 6,000^\circ \text{K.}$, about that of the sun) are necessary to bring the maximum into the middle of the visible region. Low-temperature radiation appears red,

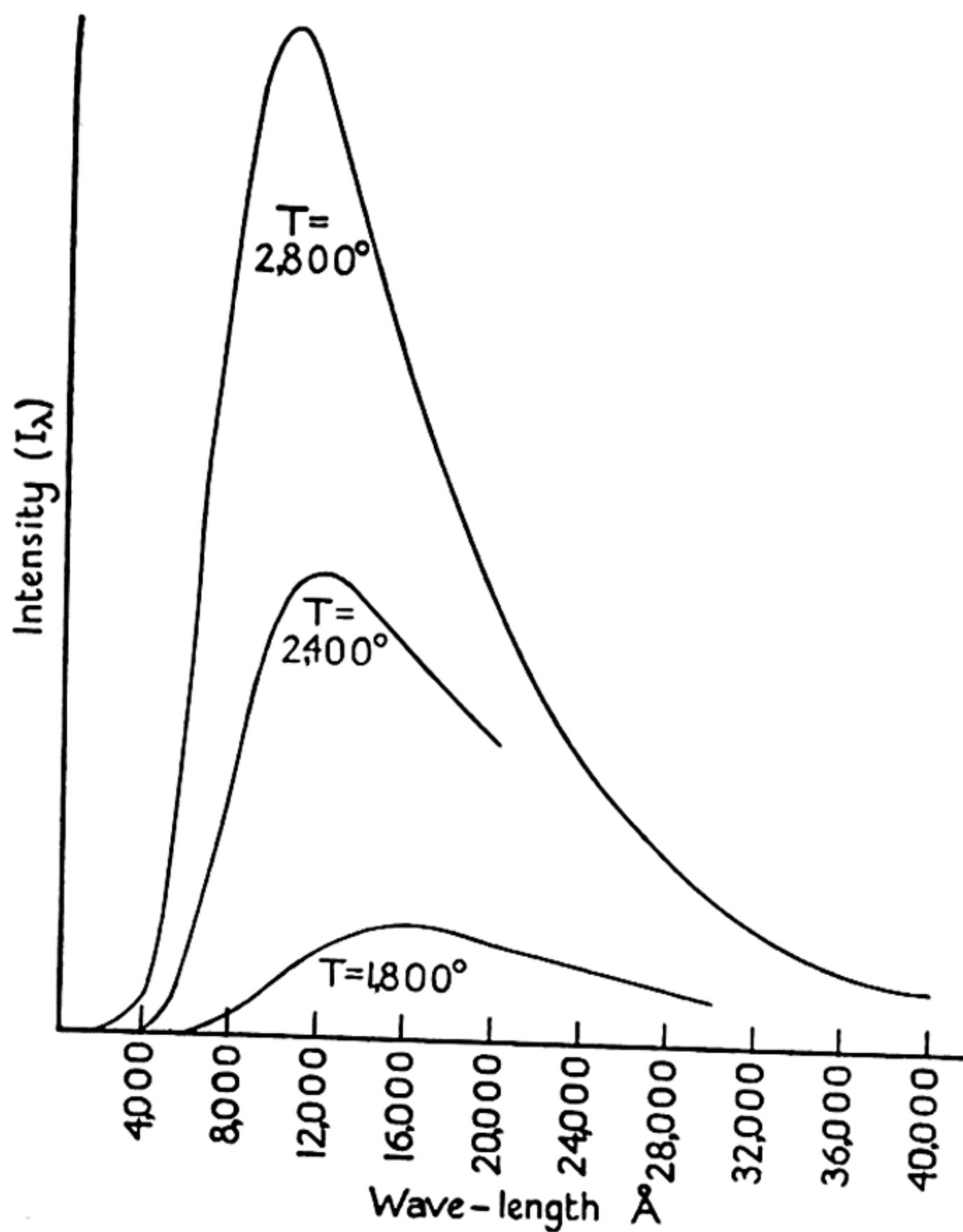


FIG. 8

becoming white at higher temperatures and finally bluish-white (e.g. certain stars). Fig. 9 shows the relative brightness to the eye of thermal sources at different temperatures and emphasizes the necessity for high temperatures to secure efficient light production in this way.

Actual solid radiators are not 'black', and their total emission is less than that of Fig. 8. As long as the emission is purely *thermal*, however, Kirchhoff's law applies, i.e. the ratio of emissive to absorptive power is a constant for each

wave-length and temperature, and equal to I_λ . One may thus distinguish between *incandescence* or thermal radiation and other kinds of light emission or luminescence. For example, the *D* lines of sodium in a Bunsen burner are *thermal* radiation by this test, while the blue inner cone is *luminescence*

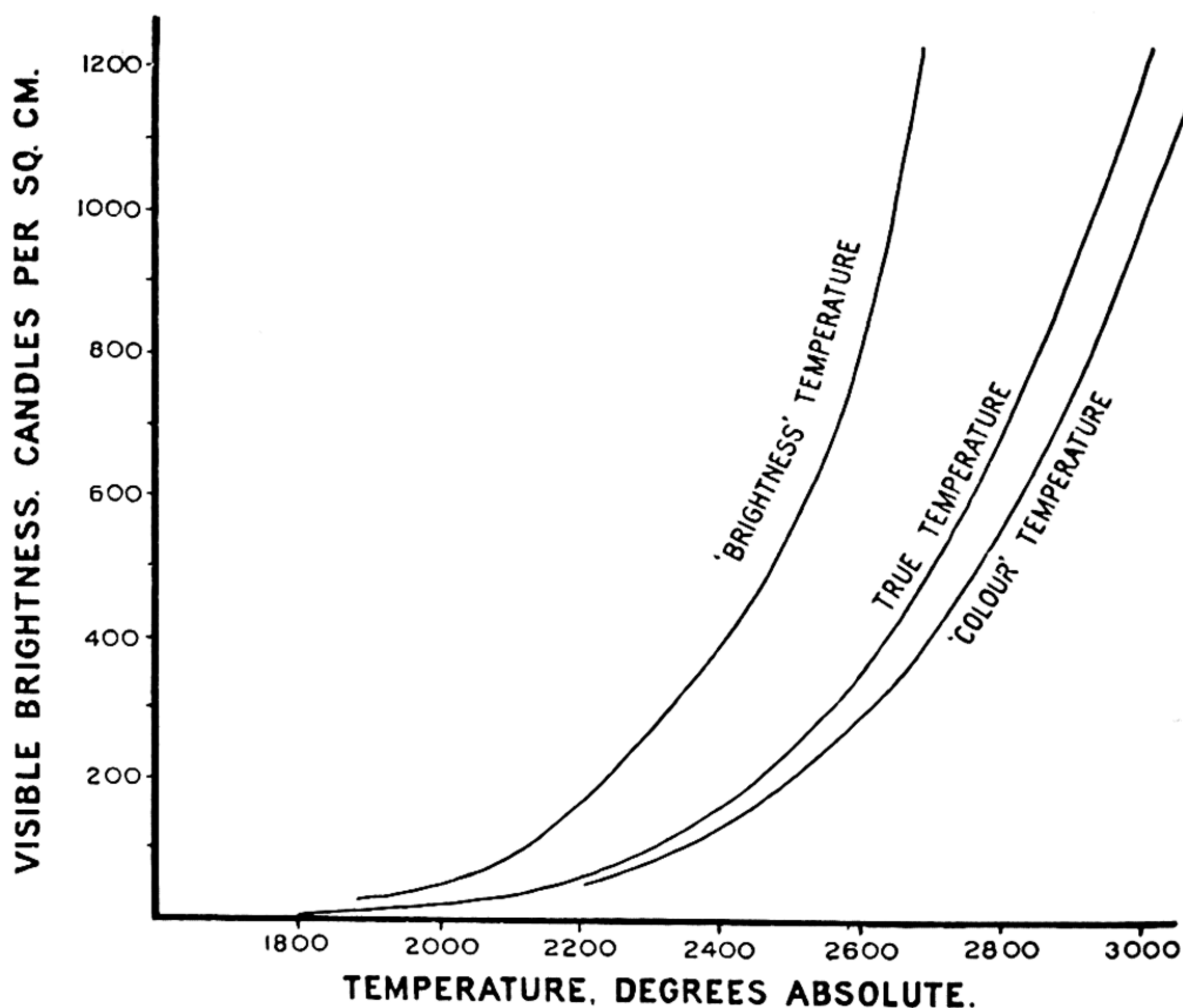


FIG. 9. 'Optical' temperatures of a Tungsten filament.

produced by chemical reaction, since the intensity of the former is consistent with the measured flame temperature while that of the latter is too great. In the latter case the radiating molecules are not in thermal equilibrium with and are 'hotter' than their gaseous environment. Non-black thermal radiators give emission curves with maxima and minima depending on their selectivity, but the ordinates always lie below those of Fig. 8. For a given rate of energy expenditure a non-black body may therefore rise to a higher temperature than a per-

fect radiator, and give the false appearance of being a better emitter if judged by its radiation intensity at certain wave-lengths. For example, carbon particles in a coal-gas flame are not as bright as a Wellsbach mantle composed of 99 per cent. thorium oxide and 1 per cent. cerium oxide; the latter material is a bad emitter in the infra-red region and therefore loses less energy there by radiation than does the carbon; it is therefore able to rise to a temperature more nearly equal to that of the surrounding hot gas. Catalytic activity plays a part in addition, the combustion reaction going faster on the oxides and the heat production there being greater. The brightness of the light from aluminium foil burning in oxygen (photoflash bulb) arises from the high temperature of the solid product Al_2O_3 by reason both of the great heat of reaction and of the poor emissivity in the infra-red region. Temperatures of bodies may be estimated from their total radiation (Stefan's law), and are called *radiation temperatures*. If estimated from the visible brightness of the emitter they are called *brightness temperatures*, or if obtained from the *shapes* of their emission curves in the visible region (nearest fit to a black-body curve in that region) they are called *colour temperatures*. Though these may sometimes differ widely from true temperatures in extreme cases, the difference is usually a hundred degrees or less for incandescent solids such as furnaces or lamp filaments (Fig. 9). It will be seen from Fig. 8 that the *ratio* of emissions at two wave-lengths defines the (colour) temperature of a radiator, and this is most commonly used for temperature measurement. Though easier than *absolute* determinations of energy, the procedure is not easy; errors arise from light losses in the instrument used for dispersing the light; the use of thermopiles as energy detectors at the high sensitivities necessary for narrow spectral regions requires delicate apparatus with elaborate precautions; the alternative detectors, photographic plates, photo-cells, and the eye have selective wave-length responses

which complicate matters. Standard electric lamps are available whose spectral distribution of energy has been carefully determined with the special apparatus necessary, and these may be employed for the determination of the temperature of other sources using relatively simple apparatus. Relative comparisons only of the two emissions are required in identical wave-length regions. Light from both sources may be passed through a dispersing system and narrow wave-length regions compared by ordinary photometric means; this is done for two or more regions. In portable *optical pyrometers* the light from a hot body is brought to a focus in the same plane as a heated carbon filament and examined with an eyepiece. The temperature of the filament can be adjusted by altering the current through it; when the image just disappears against the background of light from the hot body, the two (colour) temperatures are equal. The current-temperature curve of the filament is known from previous calibration against standard sources of known temperature. For very high temperatures, above that to which the filament can be taken, the brightness of the hot body is first reduced by the use of a red glass filter of measured transmission characteristics. Temperature may be measured optically up to thousands of degrees absolute (e.g. in stars giving continuous radiation), and is here *defined* by the radiation laws, though its ordinary definition is based on the expansion of a 'perfect gas'. Gases cannot be confined in vessels above about $1,300^{\circ}$ K. In the region where experimentally the two scales can be made to overlap they are in agreement, and their equivalence is also in accord with the quantum theory of matter and radiation. Such optically determined temperatures are of course accurate only if the body acts as a perfect radiator. *Colour* temperatures are usually greater, and *radiation* temperatures usually smaller than true temperatures.

For all purposes where instruments using *lenses* are required to give very high light intensities the intrinsic brilliance of

the light source used must be high, since an extended source cannot be focused like light coming from a point. Table I gives the brightness of some sources of visible light:

TABLE I

Source	Brightness in candles per sq. cm.
Sun (at earth's surface)	165,000
Moon	0.25
Clear sky	0.8
Hefner lamp (colour temp. 1,880° K.)	0.7
Gas-filled tungsten lamp, 2,780° K	600
Ditto, with overrun filament at 3,200° K.	2,500
Sodium lamp	10
Medium pressure mercury arc (general use)	160–1,000
Super high pressure mercury arc	20,000–50,000
Water-cooled mercury arc	60,000
Carbon arc	15,000
Ditto, high-current density	60,000
Glow-worm	0.005
CaS (Bi) phosphor 30 sec. after illumination	10 ⁻⁵

White light for scientific purposes may be obtained from a 'Pointolite' lamp (temperature radiation from a knob of tungsten *in vacuo*, heated by an arc between tungsten electrodes). For great intensity the sun, a carbon or mercury arc, or tungsten filament lamp is employed. Monochromatic light is obtainable from special sodium, cadmium, mercury, and other lamps (see Appendix I). These depend on the emission from heated vapour under high-voltage electrical discharge. Lower voltages are made possible by the use of cathodes of heated alkaline earth oxides, which emit electrons freely. Except in the case of mercury lamps the intrinsic brilliance is not high. The mercury lamp is an arc burning in mercury vapour between electrodes in a fused silica or glass vessel. If the discharge is constricted by the use of a fused silica capillary tube, the brightness is enormously increased, up to 150,000 candles per sq. cm. in the limit, but the tube, even if water-cooled, only lasts a few seconds under these conditions. A new-pattern lamp has two electrodes

reaching close together in a fused silica bulb containing mercury vapour and a little rare gas. The bulb is enclosed in an outer envelope with an air buffer between to take the pressure. The light comes from the small space between the electrodes with a brilliance of 20,000 candles per sq. cm.

For the generation of ultra-violet light down to 2,480 Å the mercury arc in fused silica tubes may be employed. Some of the lines it emits are shown in Fig. 15, and in Appendix II are given filters to transmit certain of the lines. Capillary lamps give higher intrinsic brightness. Special mercury lamps containing a rare gas, and running off a 1,000-volt supply, produce 90 per cent. of their emitted radiation in the 2,537 Å line, and afford a convenient and powerful source of monochromatic light. Light about 2,000 Å is most conveniently obtained from condensed spark discharges, and about 1,470–1,300 Å by means of special discharge tubes containing xenon. When continuous ultra-violet light is required, as for absorption spectrum work, special hydrogen discharge lamps are available which make use of the continuous emission spectrum of that substance (p. 90). Metallic electrodes (uranium or iron), which give very close-packed series of lines, are also employed.

Ordinary glass is opaque beyond 3,300 Å, and quartz beyond 2,000 Å. Thin films of glass ($10\ \mu$) are transparent up to 2,500 Å, and of fused quartz to 1,500 Å. Selected fluorite may be used to 1,400 Å, and lithium fluoride to 1,000 Å. Owing to absorption by oxygen beyond 2,000 Å a vacuum technique must be used for very short ultra-violet. Solvents for ultra-violet work comprise specially purified water, ethyl alcohol, ether, and hexane, which are as transparent as quartz in this region.

For work in which very finely monochromatic light is necessary, as when atoms are to be stimulated to excited states optically, the above sources may be unsuitable. The lines emitted by a mercury lamp, for example, are broad

owing to the high pressure of the vapour, and the centre of a line may be 'reversed', i.e. may be missing because of self-absorption of a narrow range about the atomic frequency in cooler gas near the walls of the tube. Light from a hot mercury lamp emitting a broad and 'reversed' or 'hollow' line at $2,537 \text{ \AA}$ will therefore not be absorbed by cold mercury vapour (p. 124). Special lamps may be constructed to avoid this effect, but their intensity is low.

To secure constancy of light intensity is not easy, and requires maintenance of steady electrical conditions, as well as avoidance of change of the properties of the lamp with age.

For purposes of general illumination the tungsten filament lamp is commonly used. Temperatures of about $2,800^\circ \text{ K}$. are made possible in ordinary commercial lamps by the use of gas-filling and 'coiled coil' filament winding, which reduce the evaporation of metal off the filament. Higher temperatures, with very much greater brightness, are used in special lamps where the life is of little importance. The light from tungsten lamps is much yellower than daylight; it can be approximately corrected to daylight quality by transmissive or reflective filters (absorbing the excess red and yellow) at a considerable sacrifice of the light output. Great economy in electrical power is effected by using discharge lamps such as sodium or mercury, which are more efficient light-producers. Their disadvantage is the quality of the light, which has a line spectrum and is incapable of giving proper colour rendering of objects to the eye. The sodium lamp, for example, emits only the yellow *D* lines, and red or blue objects viewed in it may appear black. All discharge lamps are deficient in red. This can be partly rectified for mercury lamps by the addition of cadmium, and still more by the use of fluorescent powders. Hot cathode lamps containing a little argon have the quality of their emission much improved by a coating of suitable zinc-cadmium sulphide preparations on the inside of an outer glass jacket. The strong Hg line $3,650 \text{ \AA}$

excites the broad emission bands of the sulphides. Alternatively, zinc silicate and magnesium tungstate preparations may be used *inside* the tube of mercury-argon or neon hot cathode discharge lamps. The fluorescence is here excited by the very short wave-lengths, which are thereby usefully converted into visible light. Efficiencies of 35–50 lumens/watt with a good approximation to daylight are obtainable in this way. Other hot cathode lamps (≈ 200 volts), such as mercury-argon, neon, or sodium, are used for coloured 'flood-lighting or road lighting (10 lumens/watt for Hg—A and Ne, 50 for Na lamps). Cold cathode discharge lamps, needing about 1,000 volts and having lower intrinsic brightnesses, find uses for advertising purposes, or, when filled with carbon dioxide, as a very efficient daylight unit for colour matching.

The comparison of light intensity, or *photometry*, is carried out in a number of different ways. Where the apparent brightness to the eye is to be determined, a visual instrument is used. By means of prisms or other optical devices the two lights to be compared are brought to illuminate a field viewed with an eyepiece. Two methods are available: the two lights can be made to illuminate the field successively for short intervals of time, equality being judged by absence of 'flicker', or they illuminate halves of the field and are so viewed side by side. The brighter light is cut down in intensity by quantitative means until the illuminations appear equal in the photometer; the ratio of brightness to the eye is then given by the extent to which the intensity of one is reduced. For this reduction in intensity use is made of distance (inverse square law for small sources), rotating sectors of variable aperture, metal gauzes of known transmission, Nicol prisms, diaphragms or apertures of variable size, or optical wedges (a plate varying in transmission by a logarithmic law from one end to the other, made either of a glass wedge of narrow angle filled with carbon black in gelatine or of an antimony film evaporated on quartz).

Instead of the eye, the thermopile, the photographic plate, or photo-cells may be used to measure light intensity. Owing to their difference in wave-length sensitivity, however, they are not generally suitable for the comparison of lights of different wave-lengths or of different wave-length distributions, except the thermopile, which accurately measures the *energy* in the light beam irrespective of wave-length, but which is not sensitive enough for use with light of low intensity. Because of the non-linear response to light of the photographic plate and under some circumstances of the photocell, the illuminations should preferably be quantitatively altered by one of the above methods until their effects on the detector are equal; and when the plate is used, it is further necessary to arrange for equal times of exposure and to confine the measurements to monochromatic lights of the same wave-length (p. 233).

Instruments to compare the intensities of the monochromatic elements of similar wave-length in two light beams are called *spectrophotometers*. The two lights are directed on to the upper and lower halves of a spectrometer slit, and are spread out into two adjacent spectra which can either be examined by an eyepiece (all the spectra being cut out by a slit except the monochromatic region chosen) or, for ultra-violet work, may be photographed on a plate. In the Hilger-Nutting spectrophotometer for the visible region the two images are brought to equality by Nicol prisms, and from the angles these are turned to the ratio of intensities is found. Such an instrument can be used to compare the spectral distributions of two light sources, or of light before and after reflection from a coloured substance, etc. Its most common application is to measure absorption spectra; for this purpose the two parallel beams of light from the same source entering the spectrometer slit are caused to pass through two identical glass cells, one containing solvent and the other the coloured solution. From a series of measurements over a wide spectral

region an absorption curve of the extinction coefficient (or its logarithm, p. 192) plotted against wave numbers or wave-lengths may be obtained.

Absorption spectrophotometry in the ultra-violet is best performed with a Spekker instrument. Here the two light beams from the same source again traverse two cells before reaching the slit of the spectrometer, and a number of photographs of the double spectra are made with different apertures of an adjustable diaphragm in the beam which passes the cell with solvent only. Points are then found in the pairs of spectra where the degrees of blackening of the plate are equal; the extinction coefficients at these wave-lengths are then calculable from the reduction of intensity by the diaphragm, the concentration of the substance, and the length of the cell. For the measurement of blackening on photographic plates of spectra use is made of a *microphotometer*. In an apparatus of this type the photographic plate is mounted in a carriage controlled by accurate screws and moved at a uniform rate past an extremely fine pencil of light rays which penetrate it and fall on a vacuum thermopile or photocell. The readings of the galvanometer connected to the latter instruments give the light transmitted over successive very small areas of the plate, and are recorded on a moving drum (covered with bromide paper and receiving the beam from the galvanometer mirror) which provides a graphical record of the 'density' of blackening of the photographic plate at every point.

The relative concentrations of coloured substances in solution are measured by *colorimeters*. Light passes up two tubes containing the liquids to be compared and illuminates the two halves of the eyepiece field. The depths of the liquids are adjusted by movable dipping plungers until the fields appear equal; the ratio of depths is then the inverse ratio of concentrations (if the extinction coefficients of the substances are independent of dilution). White light may be used,

but where the colour is feeble the illumination should be confined by filters to a band of wave-lengths within the absorption band of the substance.

The Pulfrich photometer is an instrument of great versatility. Two beams of light to be compared are received through two apertures controlled by adjustable diaphragms and illuminate the two halves of the eyepiece field. When the halves are brought to equality, the intensity ratio is given by the diaphragm readings. When used as a colorimeter, cells of fixed depth containing the solutions are interposed in the light beams. This possesses the advantage over the ordinary colorimeter in that *closed* cells can be employed. It is necessary, however, to use fairly monochromatic light with this arrangement to avoid differences of tint in the two halves of the field due to preferential absorption of some wave-lengths over others by the stronger solutions.

A very recent development in absorption spectro-photometry is the use of highly sensitive photo-electron multipliers (p. 264) in the place of photographic plates. The photo-cell is caused to traverse the spectrum and the output arranged to give a direct record of the intensities. A spectral range of 2000–12,750 Å can be covered with very good resolution.

III

THE ABSORPTION AND EMISSION OF LIGHT

MATTER AS WAVE MOTION

THE electromagnetic-wave theory of radiation is able to explain the phenomena of refraction, dispersion, scattering, reflection, interference, and diffraction in very great detail, simply by the assumptions that radiation consists of wave motion with electric and magnetic vectors at right angles to each other and to the direction of the light, and that matter contains particles of an electrical character in which induced electric dipoles are produced by the passage of the wave. It fails completely, however, to interpret a number of other phenomena, all associated with the actual absorption or emission of light by matter. One is the distribution of energy from a total radiator (p. 46), an expression for which can be derived only on the assumption that radiation is absorbed or emitted in energy units (quanta) equal to $h\nu$ ergs, ν being the frequency of the radiation and h Planck's constant. Most important, however, is the photo-electric effect, or the liberation of electrons from metals by the absorption of light or X-rays. The energy of a liberated electron is found to be $h\nu - h\nu_0$ ergs and to be independent of the intensity of the incident radiation, where ν is the frequency of the radiation and ν_0 a 'threshold' frequency. This can only be explained by assuming that a whole quantum $h\nu$ is absorbed by an atom; the energy $h\nu_0$ being that necessary first to drag the electron clear from the atomic attractions, and the remainder $h\nu - h\nu_0$ appearing as kinetic energy of the electron.

If we imagine one quantum of radiation emitted by an electron in the anti-cathode of an X-ray tube, for example, and spreading outwards in all directions, ultimately reaching a distant piece of metal, we do not find that many of the electrons in the metal each take up a little of the energy of

the wave; if any is taken up at all, the *whole energy* of the wave, however far it has got from the source, is entirely swallowed up by one single electron again. This indicates in the clearest way that radiation must be regarded as an emission of particles instead of waves. The assumption that light proceeds in small 'packets' of waves rather like particles fails because of the observed phenomenon of the interference of light over very long path differences. The 'particle-like' nature of light is again shown by the Compton effect. When short-wave X-rays (radiation from heavy metals) impinge on lighter metals they are scattered with a diminished frequency which depends on the angle of scattering. The scattering law observed proves that the radiation+electron system behaves as if there was a collision between two particles; the incident light quantum rebounds with diminished energy (lower frequency), while the electron gains energy; the physical laws observed for large objects, the laws of conservation of energy and of momentum, both being obeyed.

The basis of *wave-mechanics* is the recognition that in physics different modes of interpretation are appropriate to different kinds of measurement. There are two fundamental idealized abstract concepts in physics, that of a *particle* and that of a *wave*. A *particle* is characterized by the measurable attributes of *mass* m and *velocity* v , which can also be expressed as *momentum* mv and *energy* $\frac{1}{2}mv^2$, and it obeys the classical laws of motion. A *wave* is represented by a particular type of differential equation, and is characterized by a *wave-length* l and a *period* t .

We learn from physical experiments that *matter* often can be treated according to the laws of idealized particles; sometimes, however, as in electron diffraction, wave-theory must be used. Similarly, *light* is interpreted as a wave-motion to explain diffraction, but behaves like a particle in the photo-electric effect. Matter is measured by utilizing light, and

light by reference to matter. The interaction with disturbance of measurer and measured gives rise to the Uncertainty Principle enunciated by Heisenberg. Every *particle* concept may be related to a *wave* one, such that the product of the dimensions of the two quantities has the dimensions ml^2t^{-1} of Planck's quantum of action h . Such conjugate pairs are energy (ml^2t^{-2}) and time (t), and momentum (mlt^{-1}) and length (l). The Uncertainty Principle states that if we measure one conjugate quantity, say energy, with a precision given by the probable error ΔE , then in the same experiment we cannot measure the other quantity, time, closer than $t \pm \Delta t$, where $\Delta E \times \Delta t$ is of the order of magnitude h (or, more accurately, cannot be less than $h/2\pi = 10^{-27}$ erg sec.). Similarly, the product $\Delta(mv) \times \Delta l$ is of the order of magnitude h . When we are measuring diffraction bands, for example, we are estimating *lengths* very accurately; consequently the *momentum* of the system is so inaccurately known as to have no meaning, so that wave-theory and not particle-theory must be applied to the measurements. In experiments on the Compton effect, however, (p. 59) we measure *momenta*, and a particle theory of the behaviour of the radiation becomes necessary. Suppose we were attempting to measure with great accuracy the distance between two points with the aid of a microscope. The least detectable difference in position Δl is given by $\frac{1}{2}\lambda \sin \alpha$, where λ is the wave-length of the light employed and α is the numerical aperture of the microscope (p. 9). When the particles of matter at the two points scatter light through an angle α (by which they produce their images) it is known experimentally (Compton effect) that they suffer a recoil which changes their relative momentum by an amount $\Delta(mv) = 2h \sin \alpha / \lambda$. The product $\Delta l \cdot \Delta(mv)$ is h . If we increase the accuracy of the measurement of l by diminishing λ we effect a greater disturbance $\Delta(mv)$ of the relative momentum of the two particles. These considerations are well illustrated by the concept of

'the particle in the box' (Fig. 10). If a particle moves to and fro in a box with parallel walls, its behaviour may be treated by 'classical' dynamics, and the particle may have *any energy*, provided that the box is *large*. The equations of

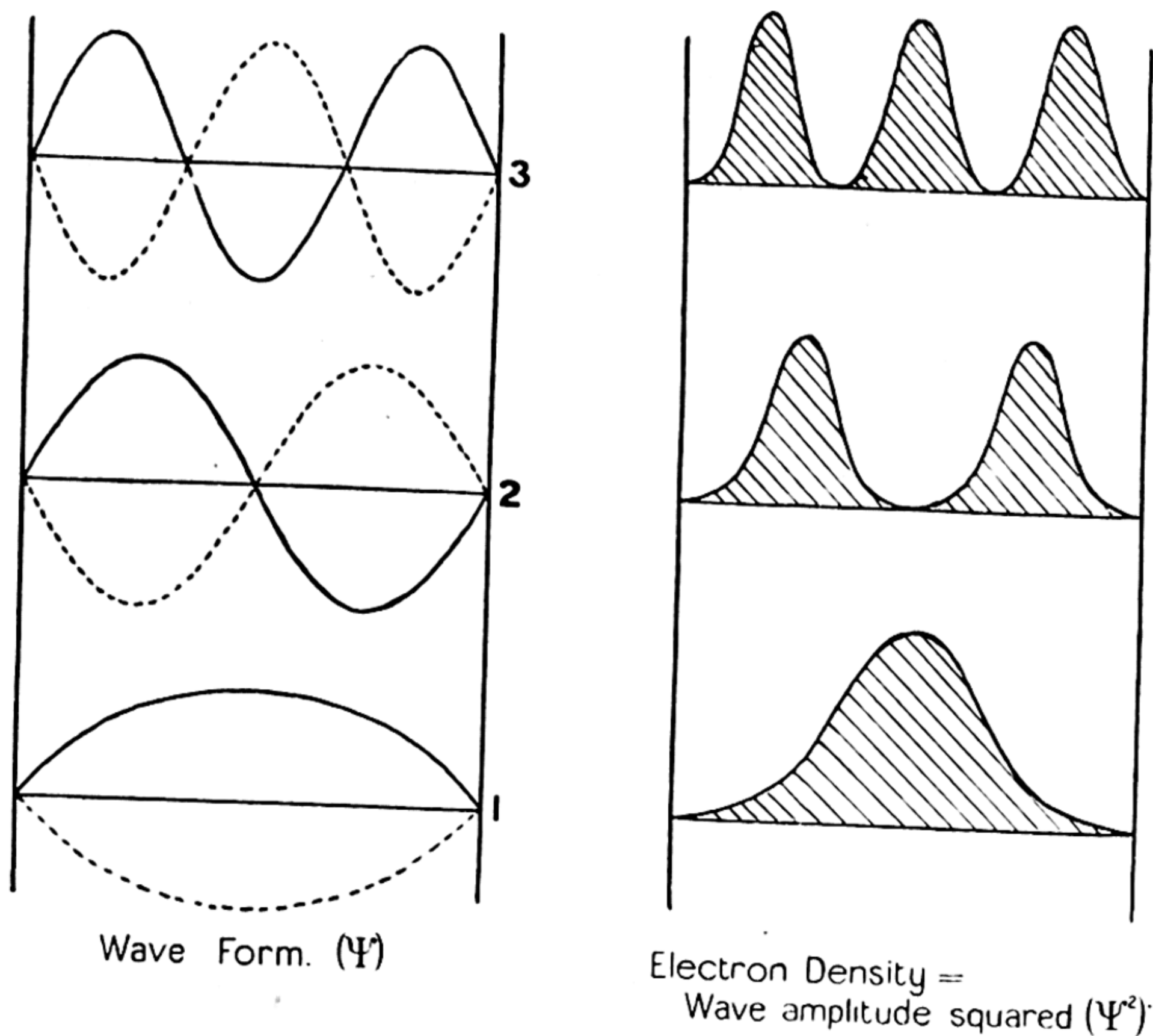


FIG. 10. Energy levels of the Electron in the Box.

wave-mechanics require us to take account of the wave-theory interpretation of the motion. The governing equations are: $mv = h\lambda^{-1}$ and $n\lambda = 2a$ where mv is the momentum of the particle, λ the wave-length, n an integer, and a the width of the box. These expressions embody the Uncertainty Principle and the assumption that if the motion has a wave character it must necessarily be a *stationary* wave, i.e. have nodes at the walls of the box, or otherwise the motion could not persist unchanged in time. The result of these conditions

is that the energy of the particle can have certain discrete values only, given by $E = n^2 h^2 / 8ma^2$, the integer n being the 'quantum number' of the energy. The reason for energy quantization is thus found in the fundamental assumptions of the Uncertainty Principle. For a *large* box the length a is not defined very narrowly, consequently we can closely define the momentum, and therefore the energy, of the vibrator. The energy 'steps' become too close to be distinguished, and the laws of the behaviour of a 'particle' apply. For a very small box the length a is very precisely defined, so that the concept of the conjugate momentum loses its meaning, and it ceases to be practicable to regard the vibrator as a particle. Instead, wave-theory must be employed. Fig. 10 shows the wave-forms of the first three quantum levels of a vibrating particle.

It is possible to attach a physical meaning to the *amplitude* (ψ) of the above wave-motion, or rather to its square (ψ^2). The square represents the *probability* that the particle will occupy any region of space. Experiment cannot establish simultaneously the exact momentum and position of the particle; if it determines the *momentum* within fixed limits, the *position* of the particle can be expressed only as a probability curve in space. Such probability distributions are called the 'particle density' curves. In Fig. 10 it can be seen that ψ^2 for $n = 1$ has a maximum in the centre of the box. This is the opposite of the result given by classical theory for a particle vibrating in a box, which is there expected to be found with equal probability anywhere across the box. For $n = 2$ there are two maxima, for $n = 3$, three, and so on. It will be observed from the shapes of the curves, however, that at high values of n the forms of ψ^2 must tend to uniform probability of position across the box, i.e. to approximate to classical dynamics, which applies when n is large.

These considerations lead us to the conclusion that when particles are relatively *unconfined* by walls or force fields they

may be treated as particles in ordinary dynamical theory; when on the other hand they are restricted in space, they must be treated by wave-theory. An electron bound to an atom is very restricted in its motion; consequently it must be treated as a wave and it is meaningless to regard it as a particle moving in any measurable sense in an orbit round the nucleus like a planet round the sun. The position of the electron in the atom can only be specified by the square of the amplitude of its wave-motion, which gives a three-dimensional probability curve called the 'electron density' for that electron. A closer specification would violate the Uncertainty Principle. The exact form of the *wave-equation*, or mathematical expression for the behaviour of micro-units of matter restricted by force fields, was first put forward by Schrödinger. It is a differential equation analogous to ordinary treatments of mechanical waves, and expresses the variation of a 'wave-amplitude' in space, the square of which represents the 'particle density' at any region. For a system of several 'particles' the equation is:

$$V\psi - \frac{h^2}{8\pi^2} \sum_i \frac{1}{m_i} \nabla_i^2 \psi = E\psi,$$

where ψ = wave function ('amplitude'),

E = total energy,

V = potential energy,

$\nabla_i^2 = \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right)$, where x_i, y_i, z_i are the cartesian co-ordinates of the i th particle in the system.

This gives the variation of ψ in *space*. ψ also varies with time t by the equation:

$$\psi = \psi_0 e^{2\pi i(E/h)t}.$$

The solutions of the above differential equation give the 'wave-motion' of the electron. These waves can be expressed in more than one equivalent way; either as stationary waves

with fixed nodes, in which case the number of nodes gives the *quantum number*, or as *running waves* with an integral number of 'wave-lengths' encircling the atom. To each set of equivalent 'waves' corresponds a fixed value of the energy E . This quantity is the *quantized energy level* of the electron concerned. It will be noticed that, although the equation above is a 'wave-equation', the 'particle' concept is partly retained. The electron is still regarded as a point charge whose coordinates in space appear in the equation and which obeys the Coulomb law of attraction applying to larger electrified bodies. A crude analogy to this 'wave' treatment is that of a stone attached to a string and flying round a centre. The ordinary laws of motion apply to the movement of the stone when its position at any instant can be measured by sufficiently rapid means. When its frequency of rotation approaches 10^{15} per sec., however, the frequency of visible light, no measuring device using such illumination will ever detect more than a blur, and the only possible treatment of the stone's movement will be a statistical one. To make this analogy more complete the Uncertainty Principle must be introduced, which excludes the possibility of improving the accuracy of the above measurements by using light of higher frequency, since this seriously disturbs the system. Since physical science deals only with quantities which can be measured, the *positions* of particles at successive *instants* of time have a meaning only under certain conditions; under other conditions one must be content with the wave concept of the motion, in which the idea of 'particle' loses its clarity and the peculiarity of energy quantization manifests itself. The equation includes within itself the mathematical form of the Uncertainty Principle, but goes beyond the principle in formulating a precise expression for the electron's behaviour in space and time. Its derivation was entirely intuitive, guided by the need to frame it to accord equally with the 'particle' and 'wave' properties of matter, and its unques-

tioned acceptance dependent on its ability to interpret phenomena more elegantly than any other rival theory. Future work will doubtless clarify some of the philosophical difficulties of the 'wave-equation' and give it a somewhat less *ex cathedra* character.

The relative spacing of the energy levels of a system given by the wave-mechanical equation depends on the potential energy term V . Fig. 11 illustrates three important cases. If r is the 'distance' of the 'particle' from the centre of the system during its movement as represented by the wave-equation, $V = Kr^\infty$ for a 'particle in a box', Kr^2 for a harmonic oscillator (e.g. two particles attached by a spring obeying Hooke's law), and Kr^{-1} for an electron in a hydrogen atom (Coulomb's law). As shown, the energy levels vary as n^2 , n , or $-\frac{1}{n^2}$, respectively, where n stands for the integral numbers 1, 2, 3, etc. For an atom with more than one electron, or molecule, $V = \sum \frac{e_i e_j}{r_{ij}}$, where e_i and e_j are the charges on any two particles (electrons and nuclei) and r_{ij} is the distance between them. In this generalized Coulomb expression r_{ij} is a very awkward function of the cartesian coordinates x , y , and z , and makes the wave-equation practically insoluble by present-day mathematics for systems of more particles than four. The equation can be applied with great exactness to the hydrogen atom, whose spectrum it completely interprets, to problems of vibration of diatomic molecules, and a few other simple cases. Applications to other atoms and to molecules cannot be made rigorously, but approximate treatments are nevertheless capable of providing illuminating results, always providing that the nature of the approximation is ever kept in mind. The following is an attempt at a simplified geometrical 'solution' of the wave-equation.

The arrangement of electrons round atomic nuclei is

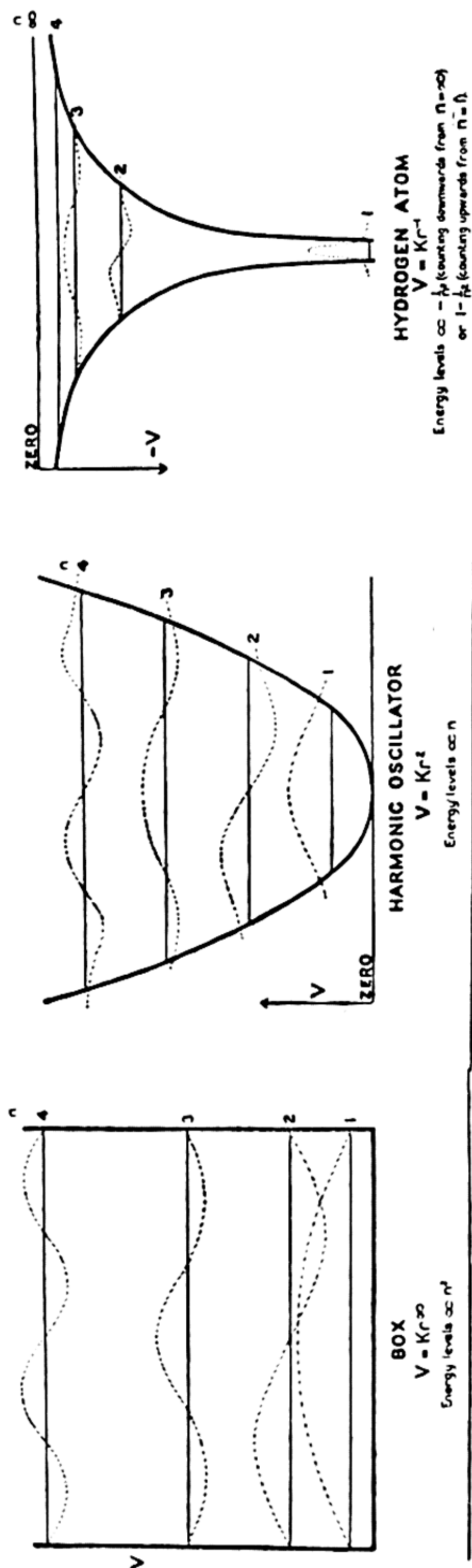


FIG. 11

Horizontal direction = distance r from centre of system.

Vertical direction = potential energy V .

Thick lines = potential energy curve in section.

Thin lines = energy levels, which are some function of the 'quantum number' n (positive integral numbers).

Dotted lines = wave-functions; amplitude plotted vertically.

governed by the 'wave-equation' which stands for a particular set of three-dimensional standing waves in space. The anti-nodes give the regions where 'the electrons are most likely to be'; one electron, however, may supposedly simultaneously be in, or divide itself between, several anti-nodal regions. To develop the matter a clear qualitative picture of the nature of 'vibrations' is required. The *fundamental* and *harmonics* in one dimension (stretched string) are easy to picture. The two-dimensional case may be illustrated by the vibrations of a drum. Here the *fundamental* is a vibration with an anti-node at the centre and a circular node round the edge. The *first harmonic*, characterized by one additional node, is somewhat more complicated, as more than one type exists. Any variety of *first harmonic* can be represented as a combination of three *normal modes*; these being vibrations of the same frequency out of which any actual vibration can be mathematically constructed. The *normal modes* are of two types, the first having a circular node separating the centre from the peripheral regions, which move in opposite phases, and the second a linear node across a diameter, the two halves vibrating oppositely. Two modes of the second type are required with their linear nodes at right angles, though otherwise in any arbitrary orientation. It is necessary to be clear about the relations of *normal modes* in the harmonics before vibrations in three dimensions can be understood.

The *fundamental* of a three-dimensional vibration about a point has spherical symmetry, corresponding to high amplitudes of vibration near the point, the amplitude decreasing outwards to a node at infinity. An electron represented by such a vibration, as the electron in a hydrogen atom, therefore has a spherical distribution of 'charge density', dense at the centre and rarefying outwards. Though the 'charge density' of the atom theoretically extends to infinity, in fact it dies away to a negligible value within an Ångström unit or so of the nucleus. This fundamental is

called a 1s orbital, the term orbital replacing the notion of 'orbit' of an electron circulating the nucleus like a planet which characterized the original Bohr theory, and the 'quantum number' 1 signifying the number of nodes. The *first*

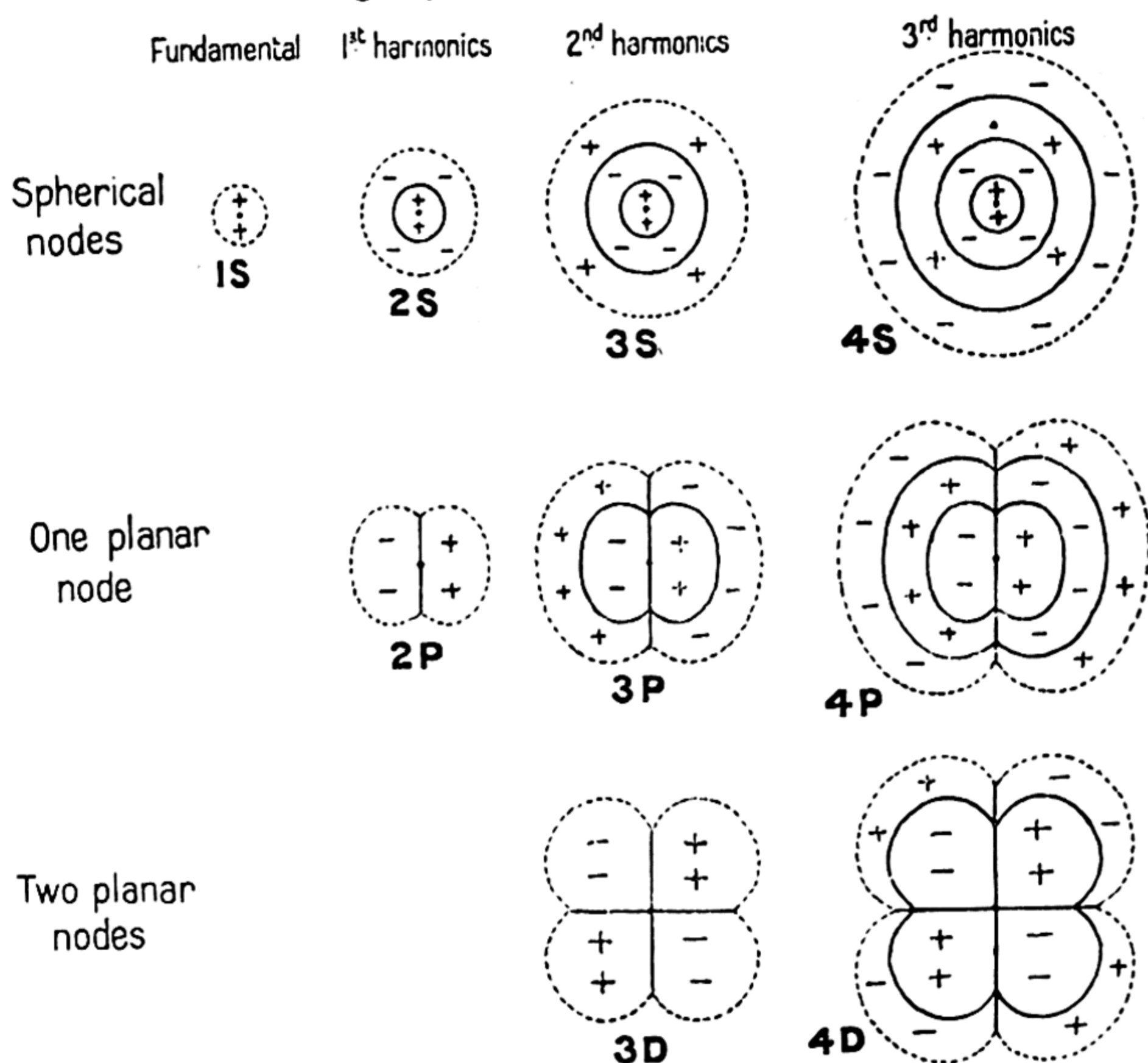


FIG. 12. Nodes of the 'waves' representing 'hydrogen-like' atoms. Full lines = nodes; dotted lines = effective nodes, actually situated at infinity. Symbols + and - refer to alternate phases of the wave-function (not to electric charges)

harmonic of three-dimensional vibrations, like that of the drum described above, may be divided into modes of two types. The first has a *spherical* node surrounding the nucleus, enclosing a region of phase opposite to that outside. The 'electron or charge density' therefore consists of an inner dense sphere surrounded by a rarefied region, this again being surrounded by a dense spherical shell. Such an orbital is called 2s. (See Fig. 12.) Higher harmonics of similar type have additional spherical nodes and their electron density

may be visualized as somewhat onion-like in character (i.e. with a concentric arrangement of shells). The second type of first harmonic has a planar node passing through the nucleus. The vibration consists of two regions of opposite phase on either side of the nodal plane, and the electron density resembles an hour-glass with a smudged-out surface. This vibration type is called $2p$, and three independent modes exist with their three nodal planes mutually at right angles to each other. Higher harmonics of p type, $3p$, $4p$, etc., have additional nodes like the higher s types, on each side of the nodal plane, so that the electron density has an overall hour-glass shape, each half divided internally into regions of high and low density so that the whole resembles a double onion. The *second harmonic* must have two nodes besides the node at infinity, and is called $3d$. Five modes of this harmonic are distinguishable, all of which on a stationary wave interpretation have two nodal planes at right angles to each other intersecting at the nucleus, three with their intersection lines parallel to the three axes of space and two of similar character with the planes rotated 45° about their intersection line. The *third harmonic*, or $4f$, represents the next stage of increasing geometrical complexity, and is divisible into seven independent modes. Higher harmonics as $4d$ or $5f$ have extra nodes dividing each part of the wave-pattern into successive curved layers. $1s$, $2p$, $3d$, and $4f$ therefore represent the lowest members of separate groups of wave-patterns; larger integers than these represent similar patterns internally divided into regions of opposite phase lying one within the other.

The equations of wave-mechanics show that the *energy* of an electron represented by any of these 'vibrations' increases with the number of nodes, i.e., with the *principal quantum number* given by the integers above. The normal hydrogen atom will therefore have its electron in the $1s$ level, while excited atoms, of higher energy, will have their electron

raised to the higher levels. The energies of levels of identical principal quantum number, e.g., $4s$, $4p$, $4d$, $4f$, are equal for the hydrogen atom so that the spectrum is comparatively simple. The spectra of atoms consist of narrow lines, i.e., they emit or absorb practically monochromatic radiation. The lines can be arranged in series, in each of which the

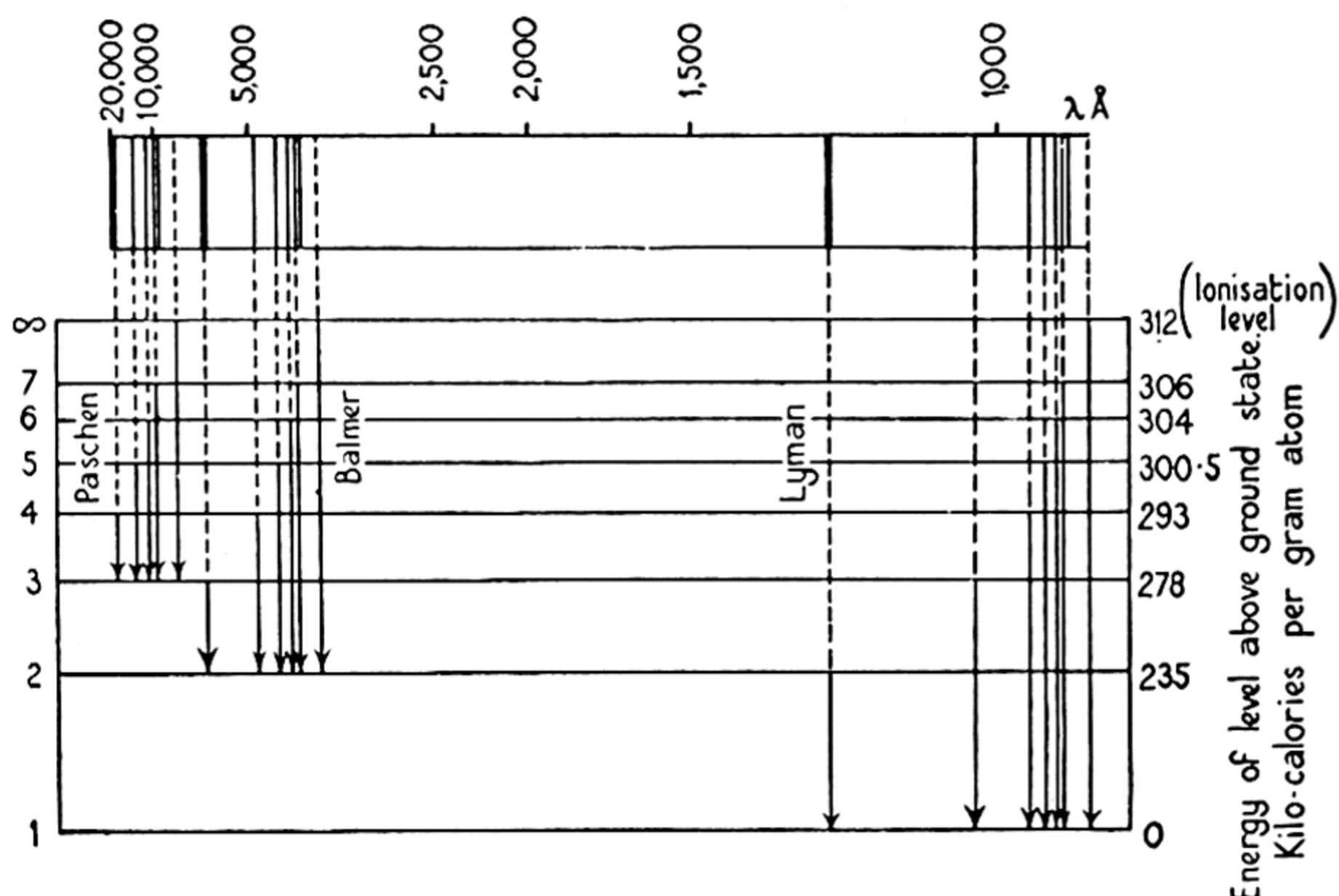


FIG. 13. Emission spectrum and energy levels of Hydrogen atom.

wave-number ω of any line is expressed by a formula as the difference between two *terms*. This is most simply shown by the emission spectrum of hydrogen atoms, obtained from vacuum tubes containing a little hydrogen gas (the molecules being split up by electron impact). Three series are shown at the top of Fig. 13; others are known further in the infra-red region. All the lines are represented by the equation

$$\omega = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right),$$

R being a constant and n_1 and n_2 integral numbers. For the Lyman series $n_1 = 1$, for the Balmer series 2, and for the Paschen series 3, n_2 being any integer above n_1 . The series converge to limits given by $n_2 = \infty$ (dotted in the figure).

The natural interpretation of a formula of this type, where the wave-numbers of lines are expressed by *differences* between two terms, is to associate the terms with energy levels the atom can assume. This step was first taken by Bohr. By passing from one energy level to another the electron in an atom emits or absorbs a quantum of radiation given by the equation

$$h\nu = hc(T' - T''),$$

T' and T'' being the *spectral terms* expressed in cm.^{-1} . At the bottom of Fig. 13 the spectral terms for the hydrogen atom are diagrammatically represented as atomic energy levels, characterized by the principal quantum numbers 1, 2, 3, etc. The ∞ level represents complete ionization of the atom into a free electron and a proton.

As unexcited hydrogen atoms at the ordinary temperature are in their lowest level, since the next is so much higher in energy compared with the average temperature energy, their absorption spectrum will be given by the Lyman series only, which lies in the far ultra-violet region.

When the wave-mechanical equation is set up for the hydrogen atom, inserting only the electron and proton mass and charge, Planck's constant h , and the Coulomb force law, and solved, it gives the exact values of the energy levels and completely interprets the spectrum. Other atomic spectra, as shown by the diagrams for sodium and mercury, are less simple. In the sodium atom four sets of levels are recognizable which may be identified with s , p , d , and f electrons, whose energies are no longer equal for identical principal quantum number. Further, the lines of the sodium spectrum show close *doublets*, while those of mercury show *singlets* and *triplets*. It becomes necessary at this stage to recognize that atoms show *magnetic* properties unaccounted for by the simple scheme of 'vibrations' outlined above. Many atoms are paramagnetic, and spectral lines are found to split into components in a powerful magnetic field (Zeeman effect),

indicating that an apparently 'single' level may really conceal more than one sub-level which can take up energy from

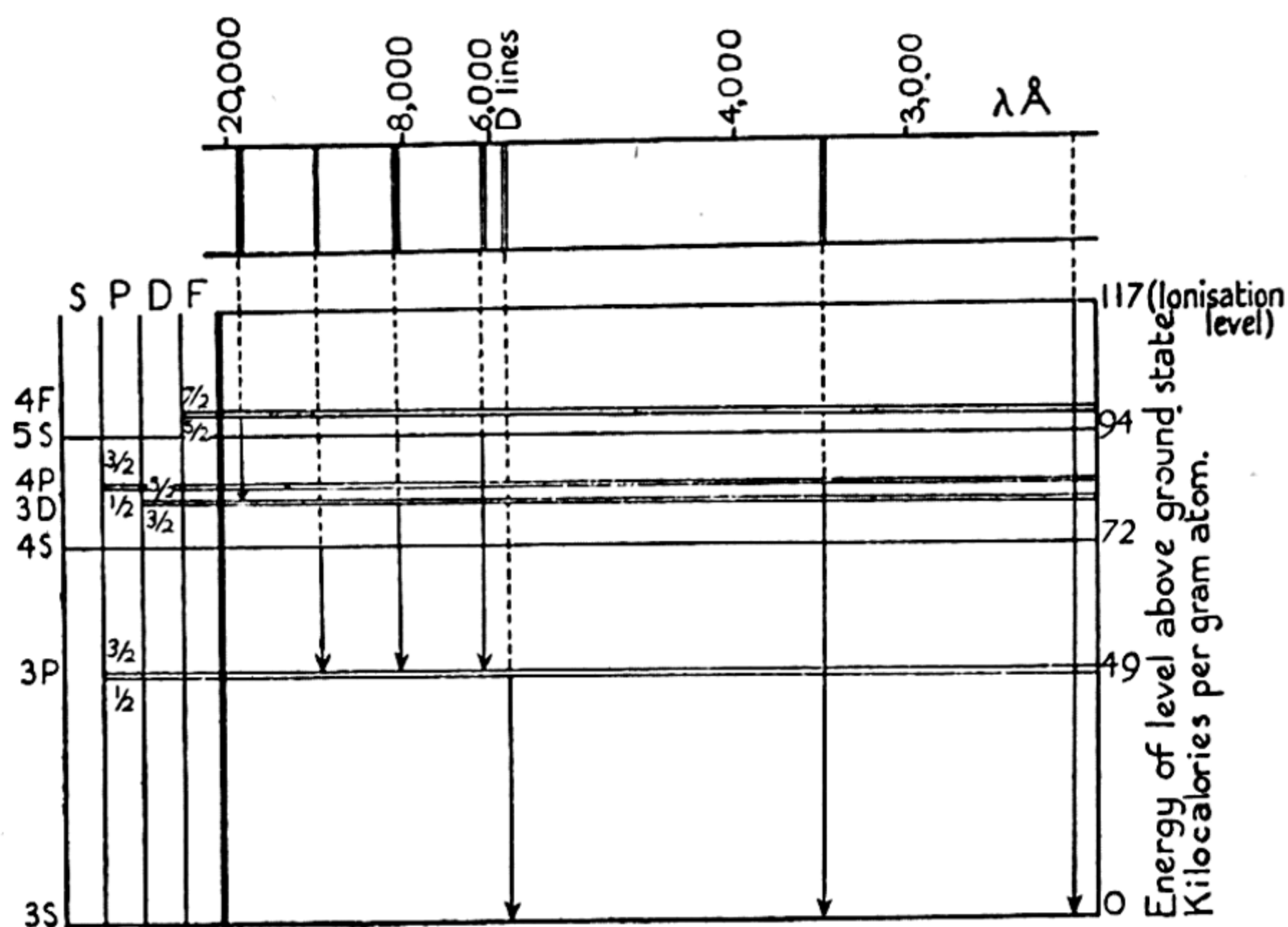


FIG. 14 Emission spectrum and energy levels of Sodium atom.

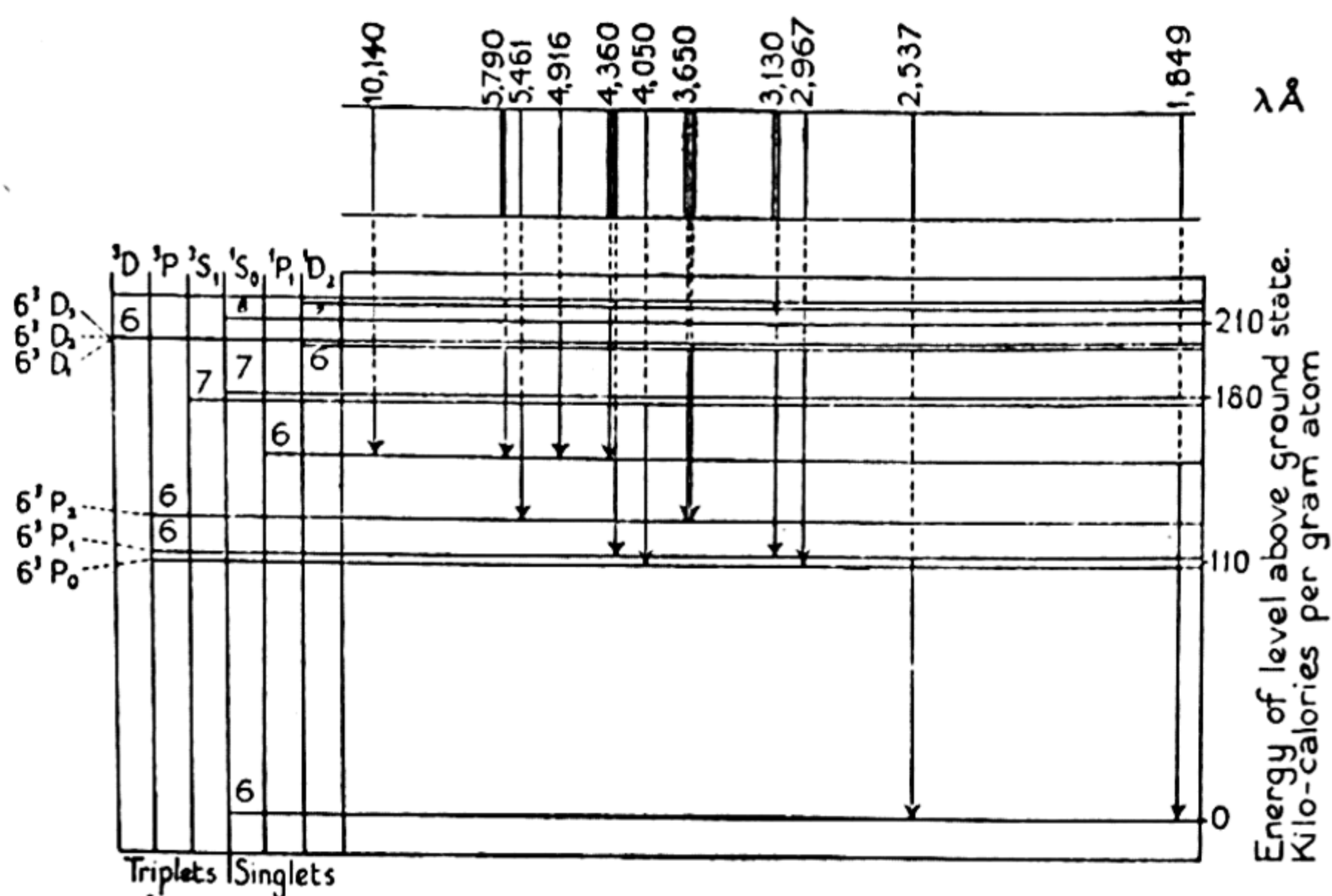


FIG. 15. Emission spectrum and energy levels of the Mercury atom.

the magnetic field in different degrees. When the wave-mechanical equations are interpreted not as *stationary* but as *running* waves, the two solutions being mathematically en-

tirely equivalent, magnetic properties appear. The *running* waves have an integral number of wave-lengths fitting round the atom, and may be pictured as waves with rotating nodes and therefore rotating anti-nodal electric charge concentrations. This treatment, however, only partly explains observed magnetic effects. It has been found necessary to assume in addition that the electron itself behaves like a little magnet of moment $he/4\pi mc$ which sets itself parallel or in opposition to the above orbital magnetism. This peculiarity is called electron spin, and is formally recognized by employing an additional quantum number which takes only the values $+$ or $-\frac{1}{2}$ (since the electron spin moment is one-half the unit of orbital moment). The doubling of the sodium lines then appears as due to the separation of the P upper level into two levels $P_{\frac{1}{2}}$ and $P_{\frac{3}{2}}$ (electron spin parallel to and opposite to the orbital respectively) whose energies are slightly different through the interaction of the inner electrons. Further splitting of levels, and so of the spectral lines, may be caused by powerful external magnetic fields interacting with the magnetic properties of the atom; powerful electric fields also cause certain levels of equal energy to separate, the energy involved of course in each case coming from the applied field.

The orbitals described above, translated into 'electron densities', are of spherical symmetry for s orbitals, hour-glass shaped for p orbitals, etc., but these 'shapes' do not necessarily represent those of excited atoms. An electron can occupy', or be represented by, more than one mode of equal energy. This is because all differential equations of wave motion are satisfied not only by one set of solutions but also by any linear combination of these solutions. An electron 'in one p orbital' is hour-glass shaped, but if it simultaneously occupies two of the three mutually perpendicular p orbitals, it will be 'smoke-ring' shaped, with a *linear* node, while by occupying all three orbitals it becomes spherical, differing,

however, from an s electron by having a *point* node at the centre. Fig. 16 shows the actual electronic 'shapes' of $1s$, $2p$, and $3d$ hydrogen-like atoms. On the right are the sub-levels distinguishable only by the effect of an external magnetic field on their energies. In the absence of a field these levels merge together to give the spherical shapes shown on the left. (The diagram cannot of course indicate the variation of electron density outwards from the atomic centres; this needs a three-dimensional model and some means of representing 'density' in space in it. The sharp edges in the diagram indicate merely where the electron density falls to a very low value outwards.)

A principle of fundamental importance in treating electrons in terms of 'orbitals' is that of Pauli. According to this, every electron in any system (atom, molecule, or larger amount of matter) must be distinguishable from every other; that is, the quantum numbers, or nodes in the full mathematical wave-function representing it, cannot be identical with those of another electron. Applied to atoms and molecules, this requires that not more than two electrons can 'occupy' or simultaneously be represented by one orbital of the kind pictured above, and if there are two they must differ in 'spin'. On this basis the peculiar arrangement of the elements in the Periodic Table may be interpreted. Hydrogen and helium atoms have one and two electrons in a $1s$ orbital respectively in their 'ground' or normal, unexcited, states. Lithium, with three electrons, must have the third accommodated in the next higher orbital, $2s$. Altogether there are four orbitals of principal quantum number 2, a $2s$ and three $2p$, and these can take up to eight electrons, covering the electronic structures of the atoms of the elements lithium, beryllium, boron, carbon, nitrogen, oxygen, fluorine, and neon. The next atom, sodium, must have its eleventh electron in a $3s$ orbital, and so on. Before potassium, with a $4s$ electron, is reached, another period filling up both the $3s$ and the three $3p$ orbitals must

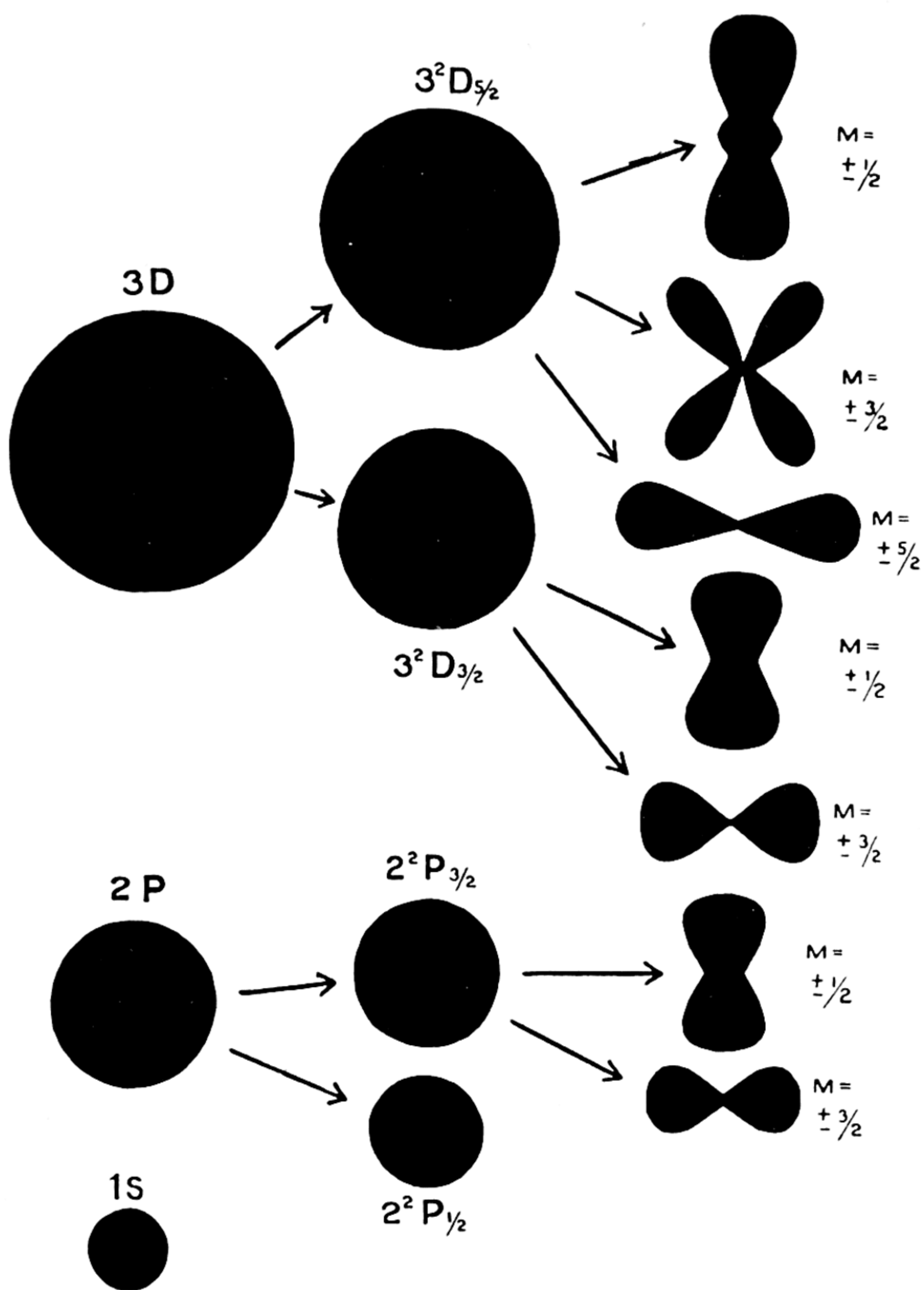


FIG. 16. Angular distribution of electron density of energy levels of a hydrogen atom. (Curves rotationally symmetric about a vertical (magnetic) axis.)

be traversed. The electronic configuration of the sodium atom is written as $1s^2, 2s^2p^6, 3s$, which is read as follows, Nearest the nucleus are two electrons in the orbital of principal quantum number 1; then we have eight electrons in orbital 2, two in $2s$ and six in $2p$ orbitals, and lastly one electron in the largest orbital, $3s$. Spectroscopically the atom is designated $^2S_{\frac{1}{2}}$, which means that the total wave-function is of S type ('second quantum number' = 0), that the level is in principle a 'doublet' (superscript 2), while the subscript $\frac{1}{2}$ specifies the particular level of the doublet. Actually, in S atoms, the doublet levels are coincident. On absorbing yellow light (D lines) the atom is excited to a higher level, the $3s$ electron entering a $3p$ orbital. The atom now becomes of P type ('second quantum number' = 1) and in one or other of the neighbouring levels $^2P_{\frac{3}{2}}$ and $^2P_{\frac{1}{2}}$ whose small energy difference shows itself in the two D lines of sodium. The superscripts are called the 'multiplicity', and equal $1 +$ the number of electrons unpaired in spin, while the subscripts, indicating the particular level of the multiplet, are given by algebraically combining the 'second quantum number' (= 0 for S , 1 for P , 2 for D , levels) with the electron spins, taking each spin as $+$ or $-\frac{1}{2}$. In a magnetic field the $^2P_{\frac{3}{2}}$ level betrays its further composite nature by splitting into four levels through the interaction of the field with the electron orbitals, while the $^2P_{\frac{1}{2}}$ level splits into two (Zeeman effect). Formally, each electron in an atom may be assigned four 'quantum numbers', the 'principal', chiefly fixing the energy; the 'second', distinguishing the S, P, D, \dots states; the 'spin' number, $+$ or $-\frac{1}{2}$; and the 'magnetic' quantum number given by the subscripts above. By the Pauli principle no electron in an atom can have an identical set of quantum numbers with another. If atoms are treated as part of larger systems, further 'quantum numbers' due to position must be invoked to satisfy the principle in its more extended form. Extending the above subdivisions due to the

peculiarities of electron spin it may easily be seen that elements in group 1 of the Periodic Table, with one outer electron, have doublet levels; elements in the second group singlet and triplet levels (the former with the two electrons spin-paired and the latter with the spins unpaired and therefore not in the same orbital); elements in the third group doublets and quartets, and so on, increasing in multiplicity towards the right of the table, and alternating with even and odd multiplicities for odd and even groups. The lengths of the periods of the table follow from the geometry of wave-motion in space, the Pauli principle, and the relative energy values of atomic levels.

The electronic configuration showing the assignment of electrons to separate orbitals is not an equivalent for the spectroscopic level. The carbon atom, for example, has six electrons, four of which are in orbitals of principal quantum number 2. The lowest level may be written as $1s^2, 2s^2p^2$, two electrons, spin-paired, in the $2s$ orbital, and the remaining two in $2p$ orbitals. There are, however, three possible $2p$ orbitals for these two electrons, and electrons can occupy more than one $2p$ orbital simultaneously. The result is that the carbon atom has more than one spectroscopic level corresponding to the above electron configuration in addition to the higher levels obtained by promoting a $2s$ electron to a $2p$ or a $2p$ to $3s$, etc.

The successive orbitals of principal quantum number 1, 2, 3, etc. have energy differences which decrease as the number increases. Except for the lightest elements, electronic shifts from the first to higher orbitals are of such high energy that they correspond to the X-ray region of the spectrum. Usually the *optical spectra* of atoms in the ultra-violet and visible region are due to electronic shifts of the outermost electrons, i.e. those of largest principal quantum number. These are often identical with the chemical 'valency' electrons. As one passes from lighter to heavier elements the wave-lengths of

the spectra corresponding to electronic transitions from any particular orbital of low principal quantum number move further towards the ultra-violet, while those due to transitions from the outermost orbital move towards the longer wave-lengths.

When electromagnetic radiation in the form of a plane-polarized light wave falls on an electron in an atom or mole-

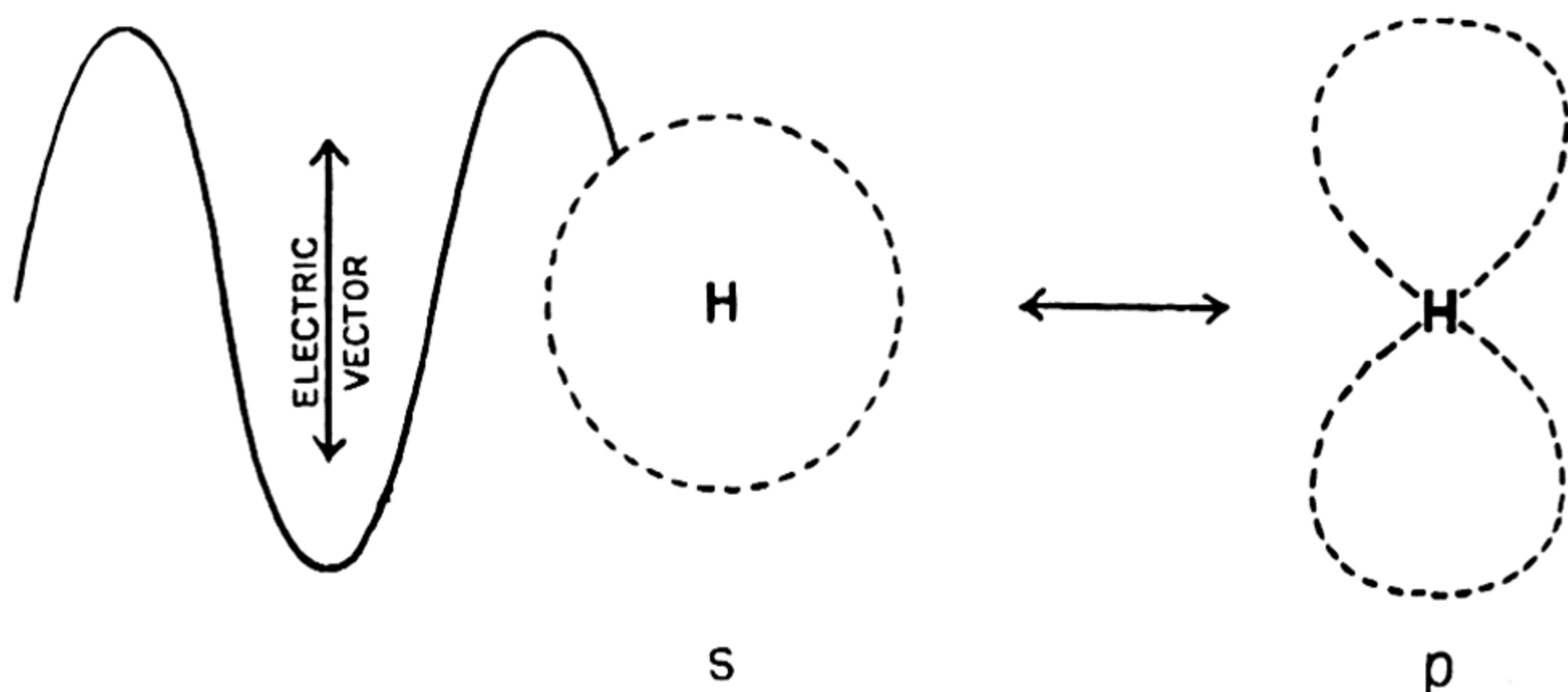


FIG. 17. Absorption or emission of light by a hydrogen atom.

cule the wave-function of the electron is set into oscillation by the electric vector of the wave. If the oscillations are 'forced', i.e. different from a 'natural' period of the electron as bound in the atom, the effect merely gives rise to the phenomena associated with the refractive index (reduction of light velocity, dispersion, etc.). At appropriate frequencies corresponding to quanta which can be absorbed by the electron the oscillations carry the electron over to a stable excited state. Fig. 17 shows this process for an $s \rightarrow p$ electronic shift. The oscillations of the electromagnetic wave necessarily cause the s electron to become a p electron with a nodal plane at right angles to the electric vector. Such a change is called in wave-mechanics 'permitted'. A shift such as $1s \rightarrow 2s$ is 'forbidden', since there is no 'dipole moment of transition', or 'electric moment matrix element' (p. 123), i.e. the wave oscillations cannot induce the change. The change $3s \rightarrow 3d$ is also 'forbidden' since the electromagnetic wave would have

to be of a 'quadrupole' character to effect it. The 'permitted' transitions are $s \longleftrightarrow p$, $p \longleftrightarrow d$, and $d \longleftrightarrow f$. 'Forbidden' transitions become partly permitted, and correspond to weak spectral bands, when the symmetry of atomic levels is distorted by near neighbours, intense fields, etc. The 'lifetime' of an undisturbed excited atom is usually about 10^{-7} seconds; after this period it re-radiates its energy. Collisions may rob the atom of its excitation energy and the energy may be converted into thermal motion (heat), so that reradiation of absorbed light usually occurs only under conditions of low pressure in the gaseous state. The 'lifetime' of the 'forced vibrations' an electron undergoes when *unabsorbed* light waves pass it is of course much shorter; about 10^{-14} seconds if the light frequency is not very near an absorption band.

Absorption and emission are entirely reversible processes; what is 'permitted' for the one is equally so for the other. Mathematically they are interpreted by the equations of wave mechanics as follows. The energy values of atomic levels are given by the solutions of the differential wave-equation. It is a characteristic of differential equations that linear combinations of the energies are also solutions. Two levels of the atom, the upper and lower (in fact *all* the possible levels), are therefore simultaneously 'included' in the equation, and the electron density is found to vibrate with time by the relation $h\nu = E_1 - E_2$, the E 's being the energies of the two levels. The fluctuating electron density 'generates' or 'absorbs' an electromagnetic wave travelling outwards or inwards respectively to the atom.

The *rates of transition* from one level to another are dealt with in wave-mechanical theory by considering the effect of radiation on the potential energy V of the system. The introduction of an extra radiation term into the equation, whose solution is taken as a linear combination of the upper and lower pair of levels considered, causes a time variation in the coefficients of the linear combination. The system thus

appears to swing from one state to the other, and the rate is interpreted as a measure of the 'life' of upper states before radiating. This 'life' is connected with the intensity (of emission or absorption) of a spectral line due to a transition, and also to its *breadth*. By the uncertainty principle (p. 60) $\Delta E \cdot \Delta t = h$, so that a finite lifetime τ of an excited state means an uncertainty in the energy difference of the upper and lower states, whence it may be deduced that $\tau = 1/\Delta\nu$, $\Delta\nu$ being the *breadth* of the spectral line. A line, in fact, is represented by a curve from $\nu = 0$ to ∞ , with a steep maximum at its experimentally observed position. Other causes also bring about line broadening, of which the chief is the Doppler effect, due to the thermal motion of atoms in the line of sight, affecting the observed frequencies as the note of a train whistle to a stationary observer depends upon the train's speed.

No lifetimes of excited states less than about 10^{-8} sec. have been observed; at the other end of the scale periods of the order of seconds sometimes occur in the case of levels from which transitions downwards in energy are forbidden.

MOLECULAR SPECTRA

Molecules differ from atoms in having more than one positive nucleus. Exact wave-mechanical treatment of the heavier atoms is impossibly difficult, and the difficulties are even greater for molecules. Only for the molecule H_2 has anything like a complete treatment been attempted. For other molecules, even though exact methods are ruled out, wave-mechanics may still be usefully applied to interpret their electronic structure and spectra.

Molecules exist in different electronic states in the same way as atoms, but their spectra are made more complex because of the quantized *rotations* and *vibrations* of the heavy nuclei. When an electronic change takes place in a molecule, changes take place in the rotational and vibrational energy,

so that absorption and emission is not confined to one wavelength but extends over a broad spectral region. Changes in electronic energy are of the order of 100 kilo-calories per gram molecule, giving spectra in the visible or ultra-violet region at frequencies about 10^{15} sec.⁻¹ The associated vibrational energy changes are about 5 kilo-calories and the rotational changes about 0.02 kilo-calories per gram molecule, and they produce the coarse 'vibrational' and the finer 'rotational' structure of the electronic spectral band. In comparison with the above energy values it may be noted that the average thermal kinetic energy of a molecule at the ordinary temperature is $\frac{3}{2}RT$, or about 1 kilo-calorie per gram molecule, and since the probability of a molecule possessing energy E is proportional to $e^{-E/RT}$, it is evident that high temperatures are necessary to produce electronic transitions by heat alone, and that at ordinary temperatures all but a few molecules will be in their lowest vibrational level, but most of the molecules will have several quanta of rotational energy.

A typical molecular *band* system is due to the many transitions (governed by selection rules) from various rotational and vibrational levels of one electronic state to those of another. The whole broad region of the spectrum (in absorption or emission) corresponds to a particular jump from one electronic level to another; it is divided up into a series of 'partial bands' corresponding to changes of vibrational quantum numbers; and very high resolution of the partial bands shows that they are composed of a fine structure of narrow lines due to simultaneous changes in rotational levels. In simple cases this triple structure can be analysed and information obtained about the molecules from which it comes. The interpretation, however, is rarely easy; it is commonly a very elaborate problem to solve; and in many cases the necessary information cannot be obtained, as the structure is absent because of molecular dissocia-

tion or because of overlapping of very great numbers of lines.

In the far infra-red region molecules absorb radiation with simple change of rotational energy. The region is extremely difficult to investigate experimentally. In the nearer infra-red molecular absorption spectra correspond to vibrational energy changes, on which are superimposed rotational changes giving a band composed of lines with a frequency difference that of the frequency of the far infra-red band. Absorption is shown only when an electric moment change occurs, e.g. diatomic molecules with two equal atoms do not absorb. Only the ground electronic state of the molecule is here involved. The moments of inertia of the molecule may be obtained from the rotational structure of the band, whence the internuclear distances (and angles) may be calculated from the known atomic masses. From the vibrational frequencies, if they can be correctly assigned to particular vibrational modes, force constants of vibration may be derived. This is very simple for diatomic molecules; more complex ones are difficult. These derived data are important molecular constants. Visible and ultra-violet spectra are complicated by the fact that each line in the spectrum depends on a transition between two electronic states of the molecule, each of which has different molecular constants. Approximately, since the orders of magnitude of the energies are different and there is little interaction between them, the energy of any molecular level $= E_e + E_v + E_r$, where E_v and E_r are energies of vibration and rotation (equal to those corresponding to the infra-red bands for the ground level of the molecule). The spectroscopic *term* of a level, proportional to the energy, may be written T (cm^{-1}) $= T_e + T_v + T_r$ and the wave number of any line in the spectrum $= T_e + (T'_v - T''_v) + (T'_r - T''_r)$, where terms with one dash refer to the upper electronic level and those with two to the lower.

For the simple case of a diatomic molecule the following

formulae apply. If m_1 and m_2 are the actual masses of the heavy nuclei, distant r_0 cm. apart, then μ ('reduced mass') $= \frac{m_1 m_2}{m_1 + m_2}$ and I , the moment of inertia, $= \mu r_0^2$. Rotational terms take quantized values given by

$$T_r = BJ(J+1) - DJ^2(J+1)^2 \text{ cm.}^{-1},$$

where J is the rotational quantum number (any integer, including 0), $B = \frac{h}{8\pi^2 c \mu r_v^2}$, r_v being the mean internuclear

distance in the *vibrating* molecule, and D a correction term to allow for the increase of this distance at high rotational quantum numbers. From the variation of B and D with vibra-

tional and rotational quantum numbers a quantity $\frac{h}{8\pi^2 c I}$,

or $\frac{28 \times 10^{-40}}{\mu r_0^2}$, somewhat larger than B , can be evaluated and

the internuclear distance r_0 for a molecule undisturbed by rotation or vibration obtained. It will be observed that the distribution of rotational levels (neglecting the D term) resembles that of the 'particle in the box' levels (Fig. 11). Fig. 18*a* shows an example of the rotational fine structure of a vibration band forming part of an electronic spectrum of a molecule. The selection rule permits of transitions only when $\Delta J = \pm 1$, and in certain cases $\Delta J = 0$. There are thus three possibilities, a decrease of 1 in J in passing from a lower state to an upper, no change in J , or an increase of 1. These produce three series of lines called the P , Q , and R branches, shown separated in the figure and marked with the changes of J on absorption. The change in moment of inertia in the passage between the electronic levels, together with the fact that the energy levels of rotation are proportional to the square of J , $\{J(J+1)\}$, produces a peculiar arrangement of these bands. The origin of the band, corresponding to a transition between two non-rotating levels (0—0), occupies the position shown in the dotted line, while the 'head' of the band, on the left

of the figure, is merely a crowding together of lines in the P branch of no significance arising from the parabolic relation of J with ν . The 'head' can be on the long- or short-wave side of the vibration band, depending on whether the moment of inertia of the upper state is smaller or larger than that of the lower. More commonly the latter is the case, as molecular distances are usually increased on excitation of the molecule. A characteristic feature of the rotational lines from molecules with two equal atoms as H_2 is the existence of 'alternating intensities' arising from the 'ortho' and 'para' forms of the molecule. These differ in the coupling of the spins of the nuclei. Ortho hydrogen has parallel spins and can take only the odd rotational states while para hydrogen has anti-parallel spins and takes the even states. At normal temperatures the proportion of ortho to para is 3 : 1. Owing to the difference of the statistics of the nuclei between hydrogen and deuterium, in the latter substance the ortho form takes the even rotational states and the ortho-para ratio is 2 : 1.

The vibrational terms of a diatomic molecule are given by

$$T_v = \omega(v + \frac{1}{2}) - \omega x(v + \frac{1}{2})^2 + \omega y(v + \frac{1}{2})^3,$$

where v is the vibrational quantum number (any integer including 0), ω (cm^{-1}) = ν/c , ν being the frequency (sec^{-1}) of vibration of the molecule at small amplitudes, and equal to $(1/2\pi) \sqrt{\frac{k}{\mu}}$, where k is the 'force constant of vibration'

(= $5.89 \times 10^{-2} M \omega^2$ dynes per cm., where M is the reduced mass in atomic weight units, i.e. $N\mu$. Cf. Fig. 11, harmonic oscillator). The terms x and y are corrections for the anharmonic nature of the vibrations at large amplitudes. Fig. 18*b* shows a simple band system. It consists of groups of 'partial bands' which can be classified into *progressions*, where the vibrational level changes by unity from band to band, e.g. transitions where the changes are $0 \rightarrow 1$, $0 \rightarrow 2$, $0 \rightarrow 3$, etc., and into *sequences*, where the transitions are $0 \rightarrow 0$, $1 \rightarrow 1$, $2 \rightarrow 2$, etc. Each transition is accompanied by simultaneous

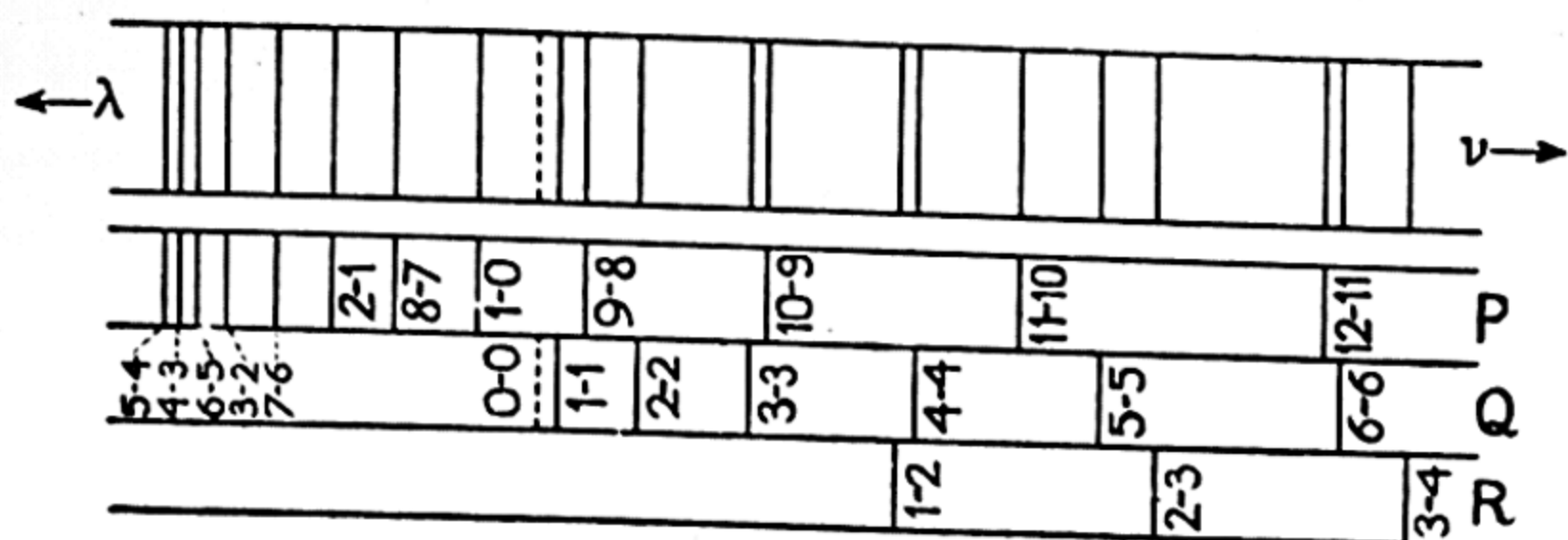


FIG. 18 a. Rotation bands of a diatomic molecule.

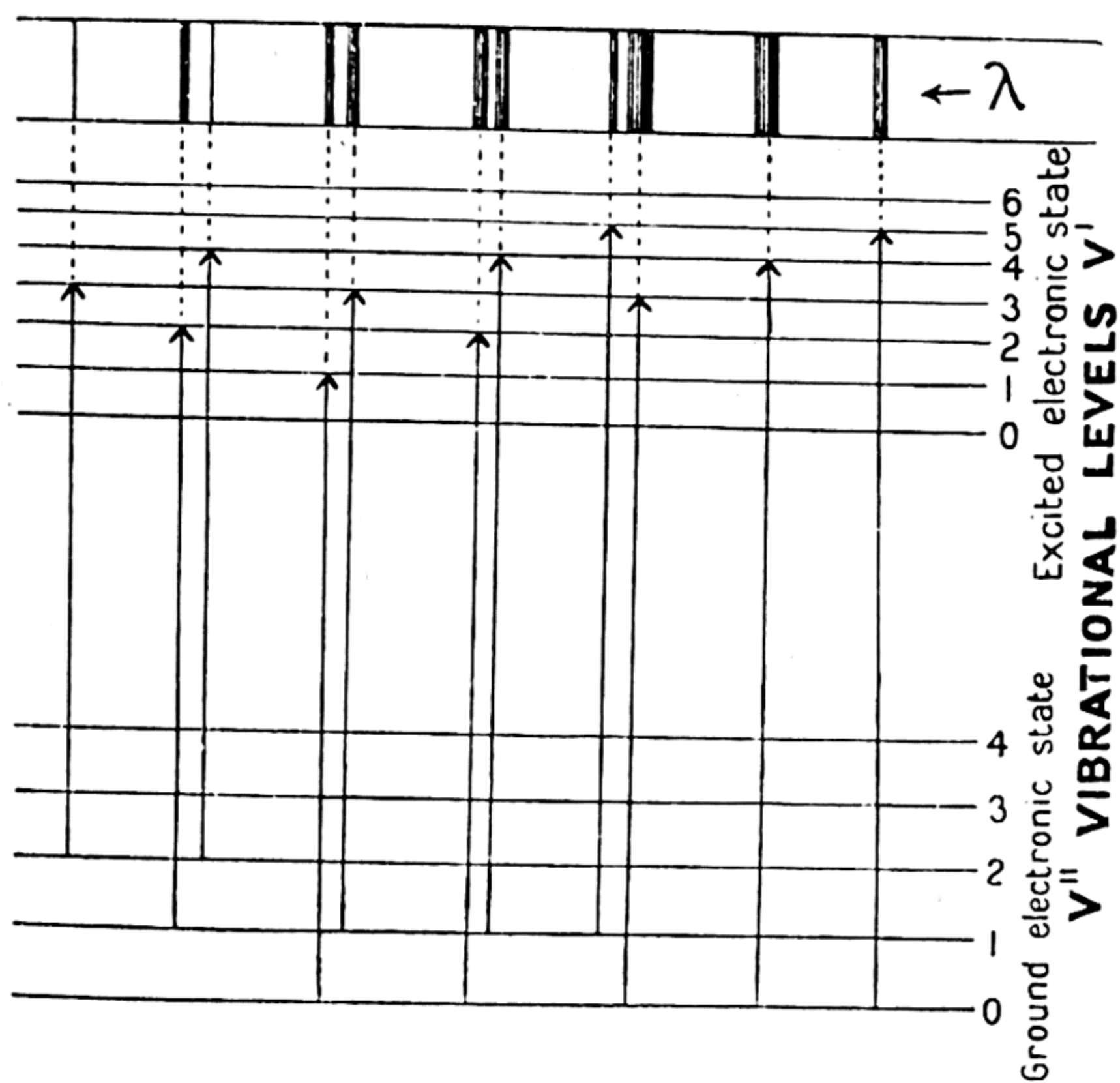


FIG. 18 b. Vibrational spectrum of a diatomic molecule.

changes in rotational levels, so that each 'partial band' corresponding to a vibrational change has a 'fine structure' of rotation bands. At ordinary temperatures most of the

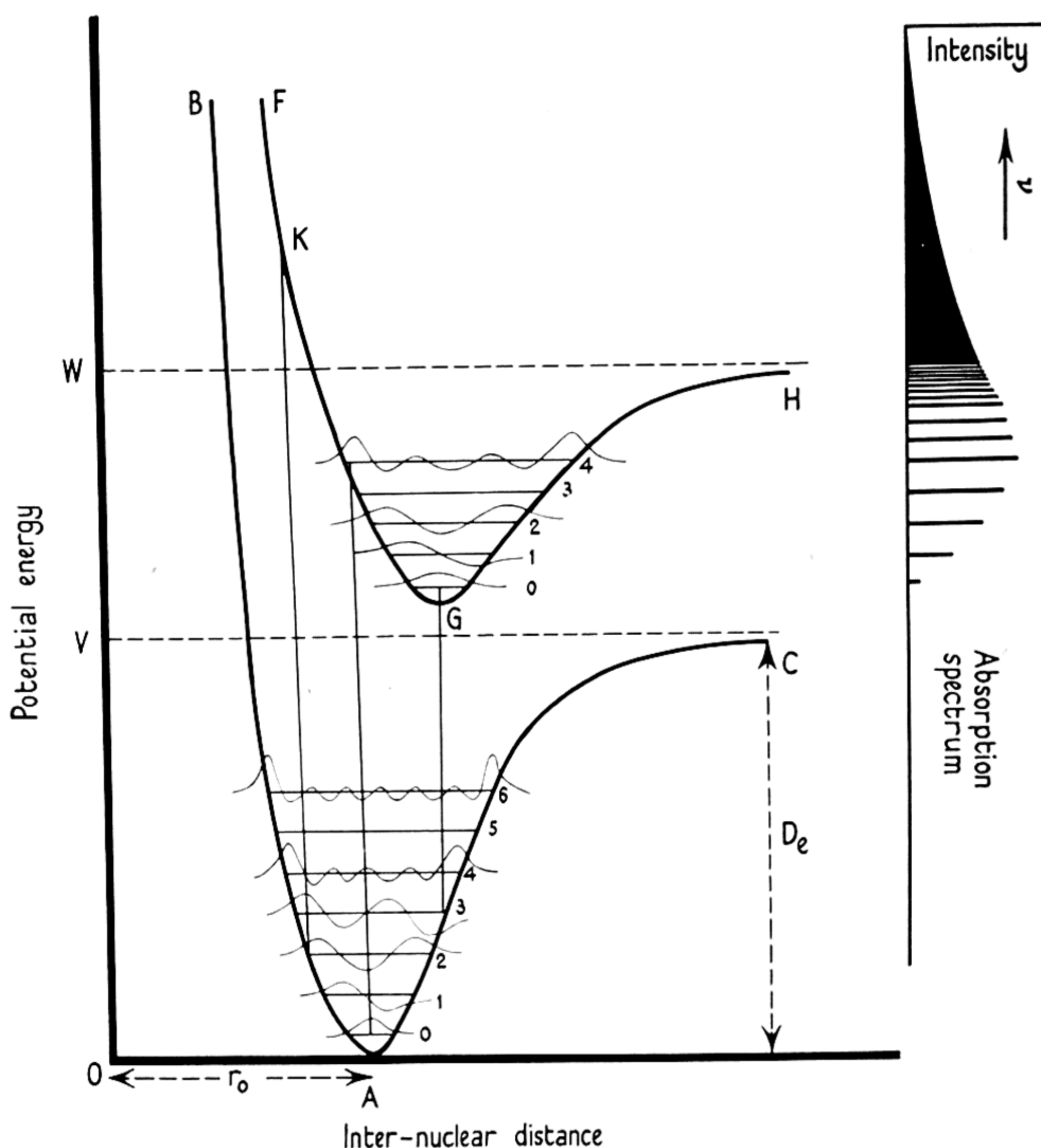


FIG. 19

molecules will be in the zero vibration level; consequently on *absorption* the most probable transitions are from that level. This is indicated in Fig. 19 by the relative partial band intensities. The bands also fade off to right and left. This intensity variation is best explained by a *vibration energy-*

distance curve, commonly called a *potential energy* curve or diagram.

In Fig. 19 the potential energy of vibration is plotted against the distance apart of the two atoms in a diatomic molecule. One atom is imagined as fixed at the axis OVW , while the other vibrates about the position shown at A , with amplitudes given by the two arms of the curve BAC . Owing to quantization of the vibrational energy the molecule can occupy energy levels shown as 0, 1, 2, 3, . . . etc. only. On the compressional side the curve AB rises steeply, but on the stretching side AC , at high vibrational energies the inter-atomic force weakens and the amplitude tends to ∞ . Consequently the height $D_e (= OV)$ corresponds to the energy of dissociation of the molecule into the two atoms in their ground states. The sinuous curves drawn on the vibrational levels are the wave-mechanical representations of the vibrations. The atomic vibrations are treated like the 'particle in the box' (p. 61) as 'waves' which give the quantum levels. The lowest level has 'half a wave' corresponding to zero-point energy of vibration of 'half a quantum' above A . This is a direct consequence of the Uncertainty Principle. These waves are represented by the quantity ψ of wave-mechanics (p. 62), applied here not to electrons but to atoms. ψ^2 is the probability of the atom being found at any point in its vibration. This is seen to be a maximum in the middle of the vibration for the 0 level, two maxima for the 1 level, etc., tending at high levels to two maxima near the ends of the vibrations with minima in between. At the higher levels the behaviour of the system is in accordance with classical mechanics, where a vibrating particle moves more slowly and is more likely to be found at the *ends* of its vibration, but at the lowest level classical and quantum mechanics give opposite results.

Above the curve BAC is another, FGH , relating to an electronically excited level of the molecule. By the absorption

of light, a molecule in the 0 level of the lower electronic state is raised to the upper state. The point it reaches is determined by the Franck-Condon principle. The electronic change is very fast compared with the vibrations of the nuclei, so that the transition must pass up a *vertical line* on the diagram. As will be seen, the maximum of the 0 level of the lower state lies below maxima of the fourth and to some extent of the third and fifth levels of the upper state. Consequently the upper excited state will be formed as a *compressed* molecule with about four quanta of vibration in this example. The *maximum absorption* will lie at a frequency corresponding to this transition. It may also be seen that absorption of light by a molecule in the 3 level raises it to point *K* above the asymptote *WH*, leading to the splitting of the molecule into two atoms which separate with *kinetic energy*. *Continuous* (i.e. structureless) spectra arise from transitions of this kind. On the right of the figure is a representation of the absorption spectrum associated with the curves. The vertical axis is a frequency scale corresponding to the energy scale on the left, and horizontal lengths represent absorption intensities. The spectrum consists of a series of 'partial bands' due to vibration level changes coupled to the electronic change, $0 \rightarrow 0$, $0 \rightarrow 1$, etc., which converge to a limit at the line *WH* and are followed at higher frequencies by continuous absorption arising from the fact that kinetic energy may be treated as non-quantized. The maximum of absorption follows from the Franck-Condon principle and the intensity falls more sharply on the long-wave side because of the curvature of *FKGH*. Each 'partial band' will have a rotational 'fine structure', and other fainter and temperature dependent bands will be present due to transitions from vibration level 1, 2, etc. of the ground state.

Potential energy curves of the type shown in Fig. 19 are obtainable with more or less precision from spectral data by considerations as outlined above. For approximate pur-

poses a useful empirical equation has been proposed by Morse:

$$\text{Potential Energy} = D_e(1 - e^{-\alpha(r-r_0)})^2,$$

where D_e is the 'chemical dissociation energy' + zero-point energy, r the internuclear distance, and α gives the 'spread' of the two arms. The 'chemical dissociation energy' is the

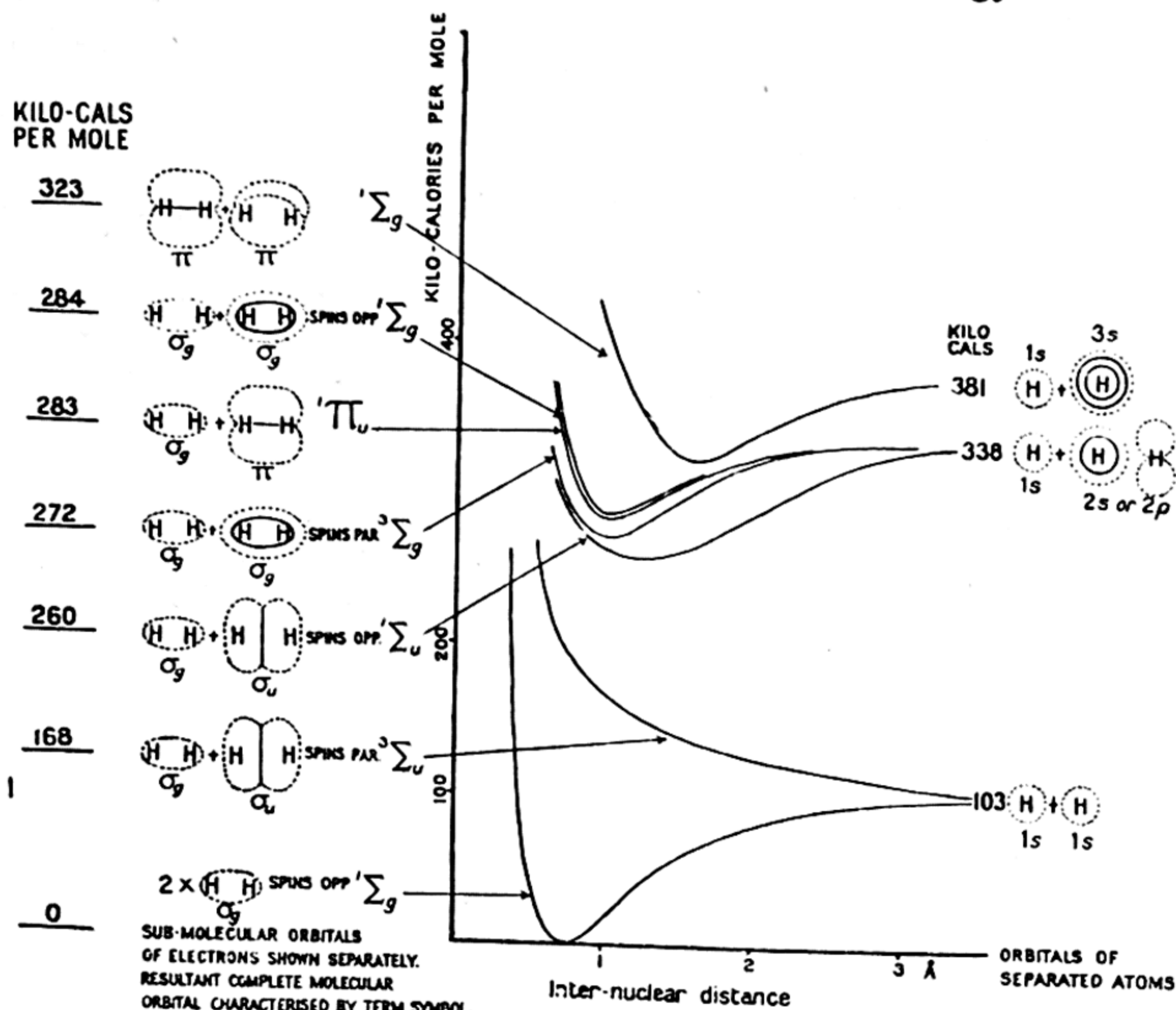


FIG. 20

quantity (VC level—zero vibration level), and is the energy necessary to split the molecule into two normal atoms. If measured thermochemically at temperatures far from the absolute zero it will differ from the spectroscopic value by specific heat correction terms, which correspond on the diagram to an appreciable fraction of the molecules starting from higher vibrational levels than the zero level. The difference is usually small.

Fig. 20 shows the potential energy curves of some of the

levels of the H_2 molecule. This molecule is peculiarly stable and over thirty excited levels are known from its emission spectrum. The electron orbitals shown at the side are discussed later (p. 103). The only transitions permitted on absorption are from the singlet ground state $^1\Sigma_g$ to the levels $^1\Sigma_u$ and $^1\Pi_u$. Transitions to the triplet $^3\Sigma_u$ level are forbidden because of change of 'spin', and to the $^3\Sigma_g$ because there is no 'transition moment'. Since the permitted transitions are to levels of high energy the absorption of H_2 lies in the far ultra-violet. Usually the *emission* spectra of H_2 are encountered. These arise by excitation (generally by electron impact in vacuum tubes) of the molecule to very high levels, from which they fall back by short transitions to generate the very complex emission spectrum of the hydrogen molecule in the visible (and ultra-violet) region. Very clean vacuum tubes, with highly catalytically active walls, favour the emission of the *molecular* spectrum and suppress the *atomic* spectrum by effecting the rapid recombination of atoms formed by dissociation. Under appropriate conditions the transition $^3\Sigma_g^+ \rightarrow ^3\Sigma_u^+$ can be observed. This differs from other transitions, which show a complicated appearance of 'partial bands' due to changes of vibrational levels, each with a finer line structure due to changes of rotational quantum numbers. In this transition a *continuous* spectrum (in the near and middle ultra-violet region) is produced, as the $^3\Sigma_u^+$ molecules dissociate into atoms with kinetic energies of any value. It forms a valuable light source for ultra-violet absorption spectrum work.

The great complexity of the energy levels of the hydrogen molecule would make it seem that those of polyatomic molecules would be too numerous to deal with. Actually, however, complicated molecules are rarely stable enough to exist in more than one or a very small number of electronic configurations.

Fig. 21 shows molecular levels of oxygen. 'Forbidden'

transitions, allowed to occur to a slight extent by the disturbance through collisions of the exact symmetry properties of the molecule, are observed between the ground level $^3\Sigma_g^-$ and neighbouring ones $^1\Delta$ and $^1\Sigma_g^+$; these give rise to faint absorption bands (in the infra-red and visible region) ob-

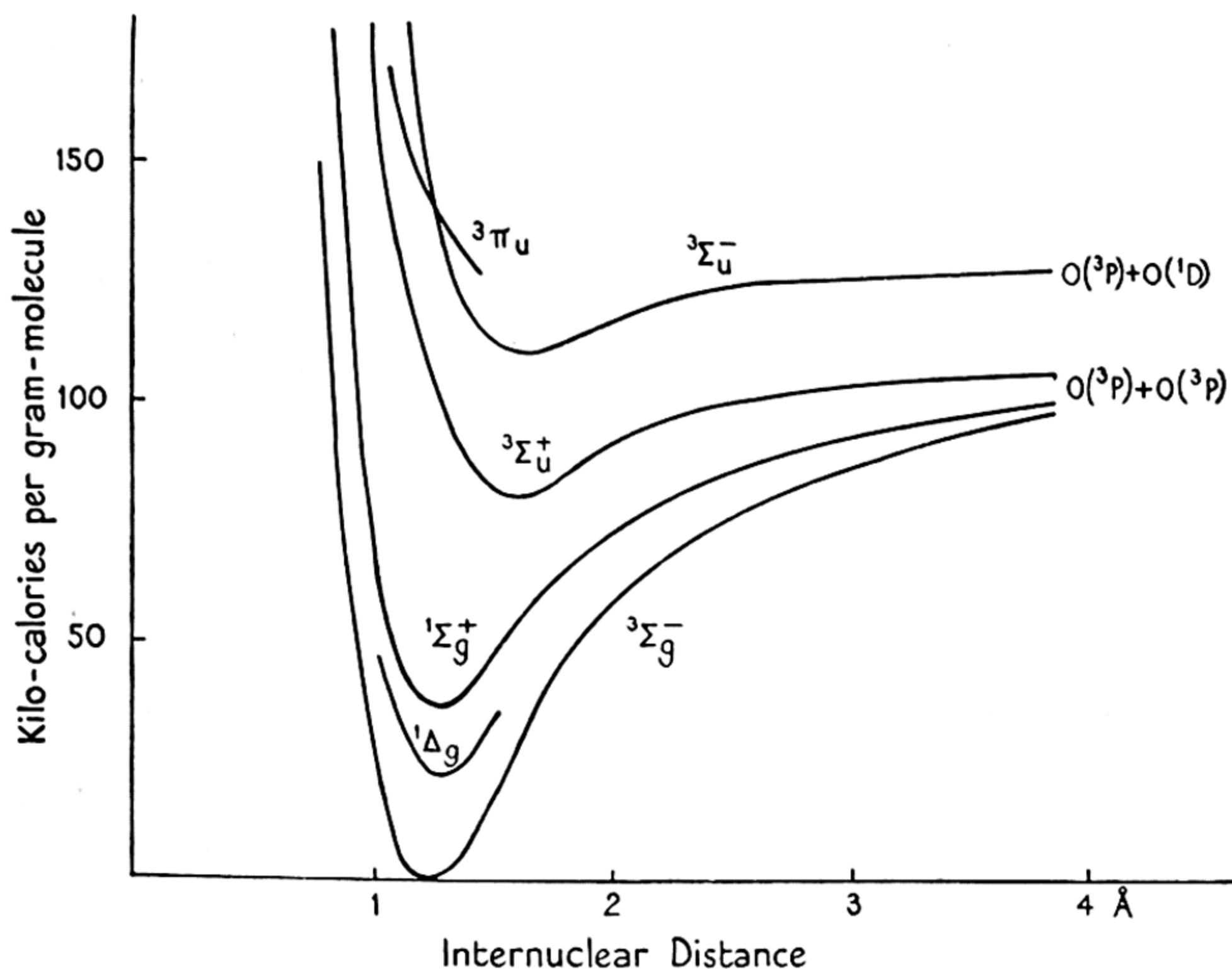


FIG. 21

served in sunlight which has passed through the earth's atmosphere. Absorption in the ultra-violet region produces the $^3\Sigma_u^+$ and $^3\Sigma_u^-$ (or $^3\Pi_u$) levels, which dissociate into atoms if they have sufficient energy. These transitions are 'forbidden', and are therefore not characterized by very strong light absorption. There is some uncertainty about the interpretation of experimental data referring to this region.

The absorption spectrum of chlorine is of special interest because of its relation to photochemical problems. Its interpretation by Franck afforded the first and the clearest

explanation of how molecules may be dissociated by light. At the ordinary temperature Cl_2 molecules are in various rotational levels of the lowest vibrational levels of the $^1\Sigma_u^+$

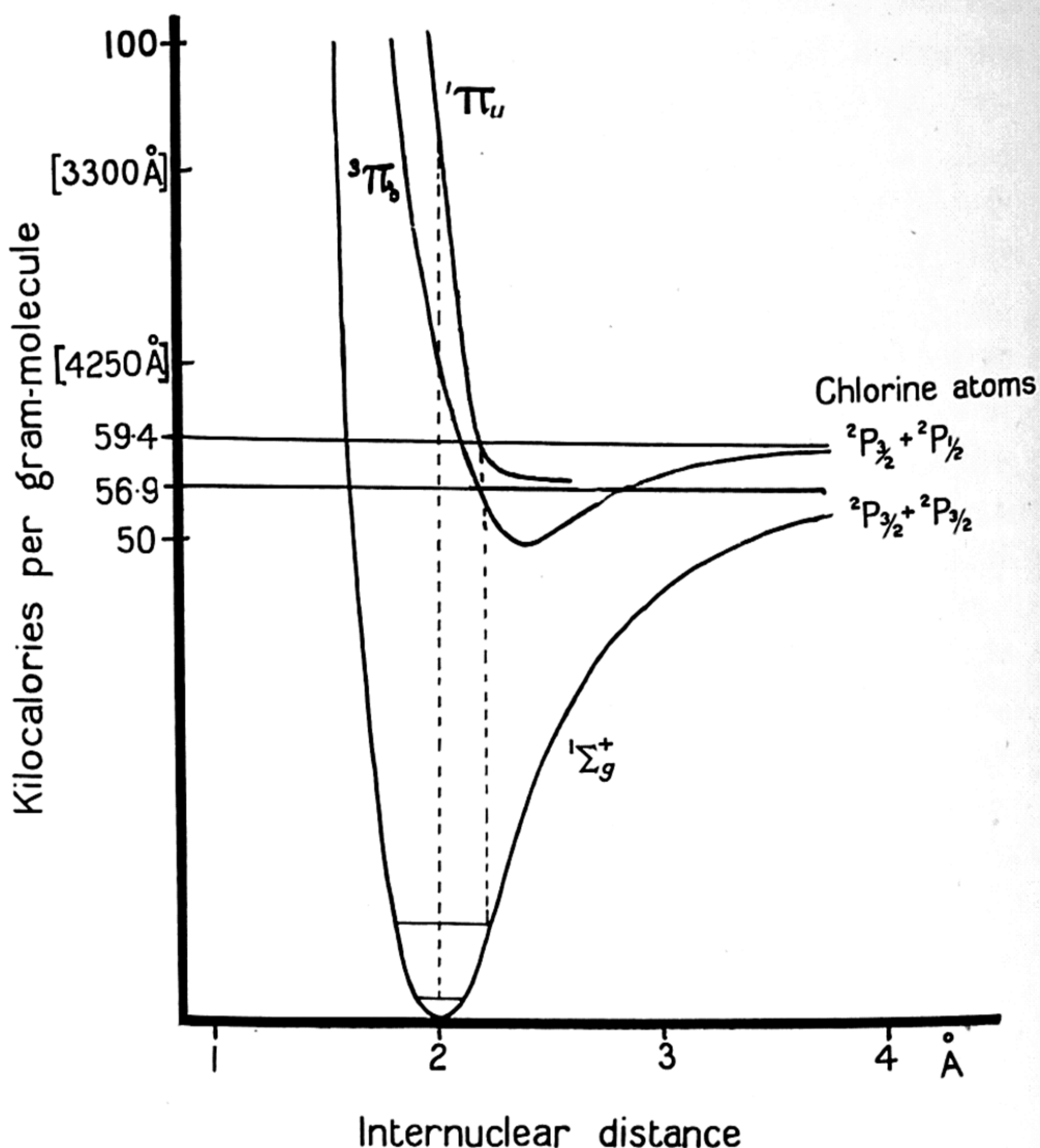


FIG. 22

electronic state, i.e. near the minimum of the lower curve of Fig. 22. On the absorption of light we must imagine the molecules as starting from near the bottom of the $^1\Sigma_g^+$ state and jumping to an upper state by paths represented by the dotted vertical lines (Franck-Condon principle). Where the vertical lines cut the upper state curves the intensity of absorption is a maximum (3,300 Å and to a lesser extent

4,250 Å), since these are the *most probable* transitions. It will be seen from the figure that absorption near 3,300 Å gives a *highly compressed* $^1\Pi_u$ state which on the very first outward vibrational swing dissociates into two normal chlorine atoms ($^2P_{3/2}$). The spectrum here is *continuous*, corresponding to the variable non-quantized kinetic energies possible for the separation of the atoms. Absorption in the blue region of the spectrum, where the extinction coefficients are much smaller, causes a transition to the $^3\Pi_{0u^+}$ state, whose dissociation products are a $^2P_{3/2}$ and a $^2P_{1/2}$ atom; the energy of dissociation being 59.4 kilo-calories instead of the amount 56.9 for dissociation into normal atoms. Those molecules which pass to the state by absorption of wave-lengths shorter than 4,785 Å (59.4 kilo-calories) photodissociate into one normal and one excited ($^2P_{1/2}$) atom. At longer wave-lengths non-photodissociating vibrational levels of the excited molecule are reached. The spectrum is continuous at shorter wave-lengths than 4,785 Å, but at wave-lengths longer than this limit it consists of vibrational bands with their associated rotational fine structure. From this spectroscopic limit where the vibrational bands converge the heat of dissociation of chlorine into a $^2P_{3/2}$ and a $^2P_{1/2}$ atom can be very accurately obtained; subtraction from this quantity of the energy of excitation of the $^2P_{1/2}$ atom (from the emission spectrum of chlorine at low pressures) gives the normal heat of dissociation of chlorine. Molecules excited by wave-lengths in the banded region at excitation energies between 59.4 and 56.9 kilo-calories cannot dissociate *spontaneously*, since they have insufficient energy to give one $^2P_{3/2}$ and one $^2P_{1/2}$ atom, though they have a greater energy than two $^2P_{3/2}$ atoms. By collision with other molecules, whereby the curves of the levels are distorted by the strong atomic electrical fields, these $^3\Pi_{0u^+}$ molecules may pass over to the $^1\Pi_u$ level and dissociate into two normal atoms. This secondary process is an *induced predissociation* (p. 96). Bromine and iodine have

absorption spectra of similar characteristics. Their convergence limits, 55.6 and 56.8 kilo-calories, are close to that of chlorine, but they have lower heats of normal dissociation (45.2 and 35.2 kilo-calories), owing to their larger atomic

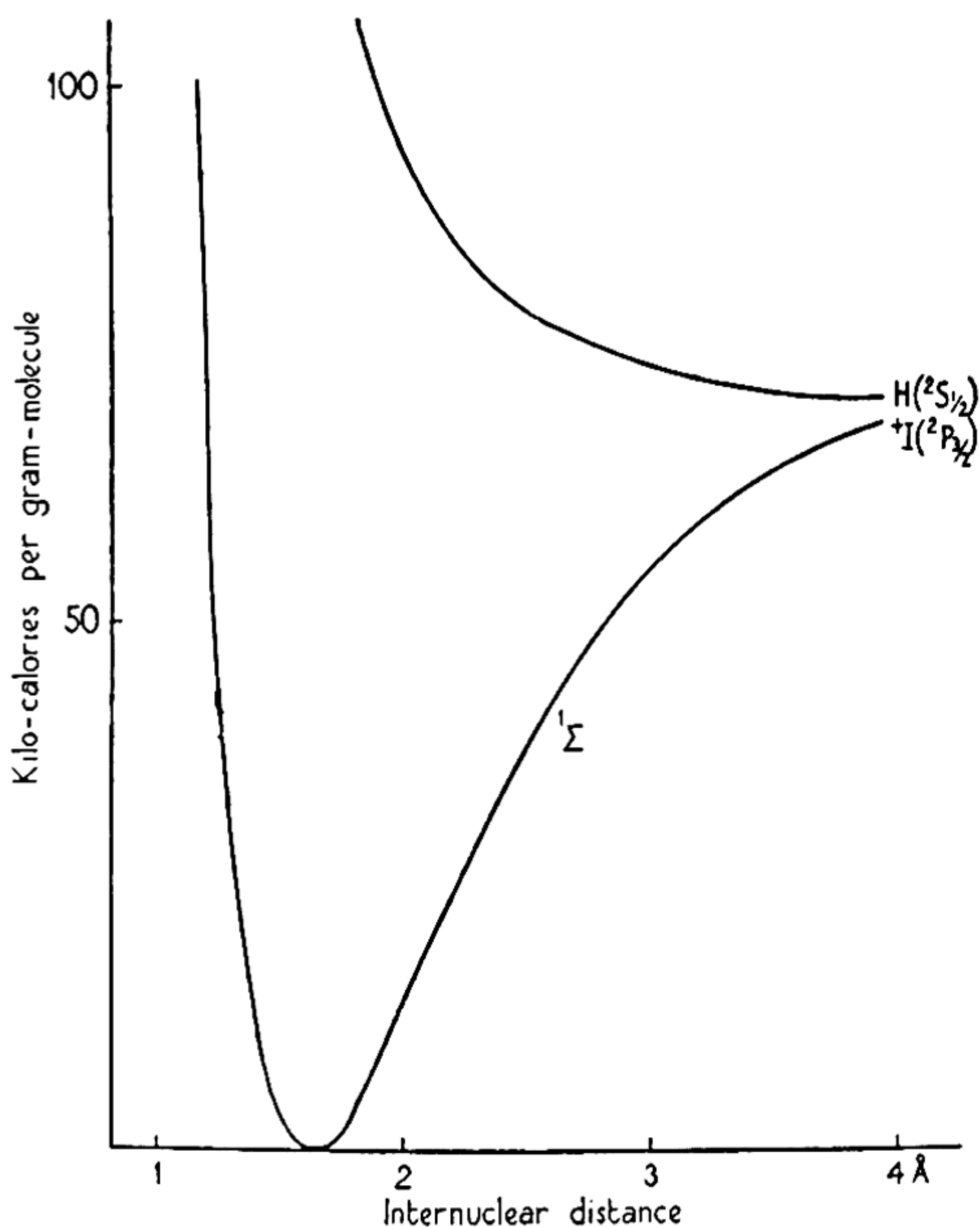


FIG. 23

excitation energies. They have therefore wider ranges of potential induced dissociation.

The potential energy curves of hydrogen iodide are shown in Fig. 23. The upper level is repulsional, and the absorption band structureless. Photodissociation into atoms, both in their ground level, always occurs on absorption. The long-wave edge of the band (about 4,000 Å) corresponds to the calculated energy value of this process of dissociation; hence the assumption of the type of curve shown.

The curves for the S_2 molecule (Fig. 24) bring out other spectral characteristics. The absorption band has a sharp structure from its beginning about 4,100 Å to 2,799 Å. Beyond this point the rotational fine structure becomes blurred, but the spectrum is not continuous, as the coarser vibrational

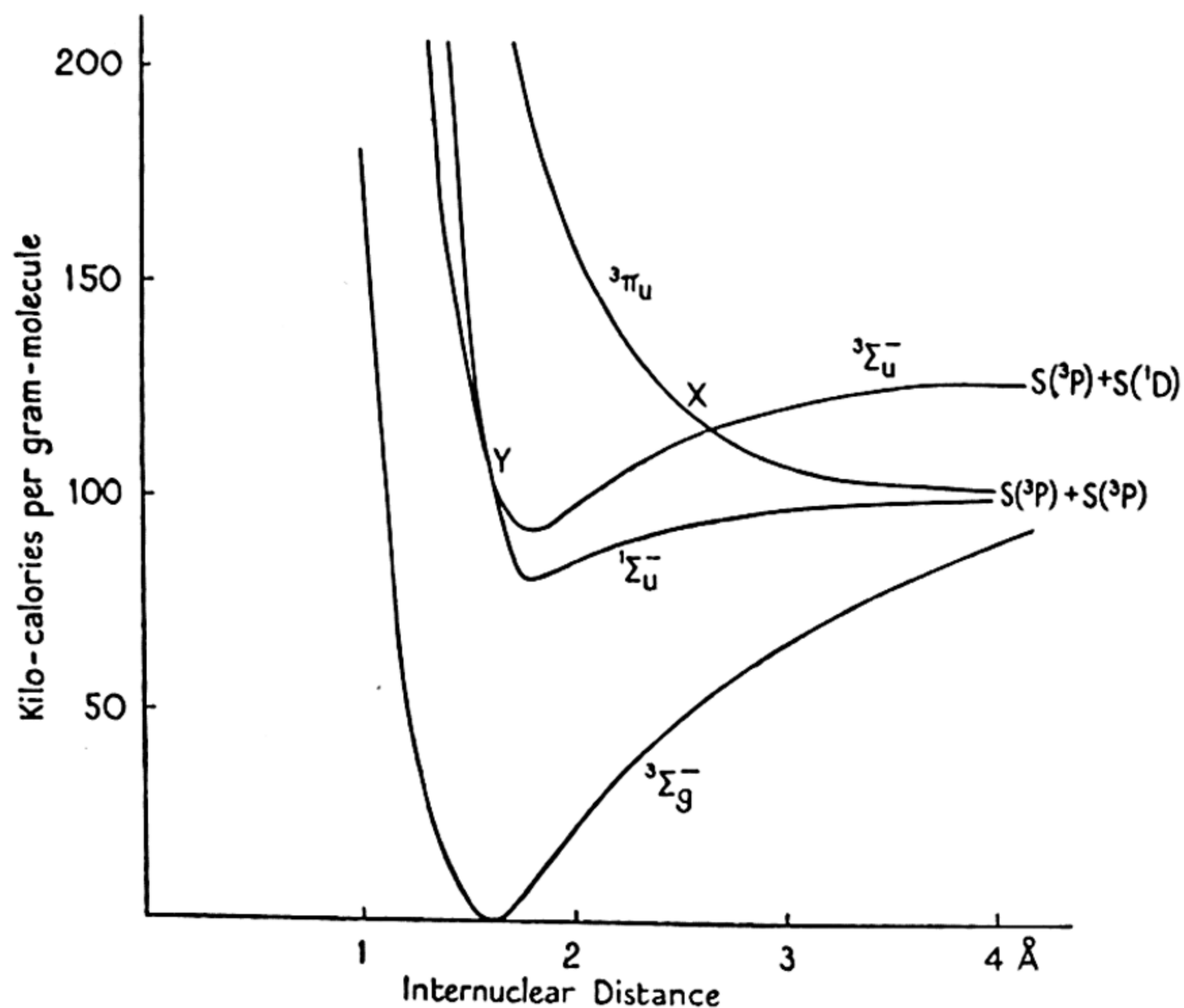


FIG. 24

structure remains. After 2,715 Å the rotational lines become sharper, but at 2,615 Å are again blurred out. The first diffuse region is affected by pressure, the blurring not occurring at very low pressures, but the second region is always diffuse. This blurring of rotational fine structure is commonly associated with a dissociation of the molecule, not occurring immediately, but after a period longer than a vibrational period ($\approx 10^{-13}$ sec.) and shorter than a rotational period ($\approx 10^{-11}$ sec.). The rotational structure thus disappears to a greater or less extent, but the vibrational bands remain. Such a delayed process is called *predissociation*, not

a very happy term. As the actual blurring is also called by the same term, we will avoid confusion by naming this spectral predissociation. The electronic change occurring in the S_2 molecule on absorption is a jump from a $^3\Sigma_g^-$ to a $^3\Sigma_u^-$ level. Absorption in the second, non-pressure-sensitive diffuse region, causes the molecule to vibrate at energies near the horizontal line through X . The molecule executes a number of vibrations, and then passes through the crossing-point to a repulsional $^3\Pi_u$ level, which at once dissociates into two normal atoms. This behaviour is styled true predissociation. At lower energies of excitation, near Y , the $^3\Sigma_u^-$ curve crosses that for $^1\Sigma_u^-$. A direct passage between the curves, however, is forbidden by the selection rules. Collisions, by distorting the levels, permit the change and consequent dissociation; hence the pressure sensitivity of the diffuseness. An effect of this kind is called *induced predissociation*.

According to the strict considerations of wave-mechanics it is not correct to visualize potential energy curves as actually 'crossing'. When two curves approach one another, wave-mechanics predicts a change from one to the other with a low frequency comparable with the vibrational frequencies. Under these circumstances the total energy of the molecule is no longer separable into three terms $E_e + E_v + E_r$. The energy-distance relation loses its precision and the 'point of crossing' (or of near approach) becomes an indefinite region.

The interpretation of the absorption spectra of polyatomic molecules presents great difficulties. Many of them are diffuse or continuous. A polyatomic molecule of n atoms can vibrate in $3n - 6$ modes. Its representation needs potential energy *surfaces* in many-dimensional space. Attempts to elucidate the vibrational modes from the observed bands are complicated by the anharmonicity of the vibrations, whereby they couple together and cause the molecule to execute intricate Lissajous figures over its potential energy hypersurfaces. Mechanically this means that each chemical link in the

molecule does not vibrate independently; the vibrations interact, and the energy passes to and fro through the molecule in a very complicated manner. The possibility of 'predissociation' occurring is thus increased, since the molecule passes through phases where the bulk of the vibrational energy finds itself on one link. The inadequacy of the spectral data may be supplemented by a study of the photochemical changes produced, but the results are never simple. The wave-length where spectral predissociation (induced or otherwise) sets in gives an approximate figure for the energy of rupture of the link which breaks. Owing to the frequent lack of sharpness in the onset of diffusion in the spectrum, to lack of knowledge of the forms of the potential energy surfaces, and to considerations mentioned below, where it appears that diffuseness does not always indicate dissociation nor fine structure absence of dissociation, great accuracy or even certainty of interpretation is impossible; but if the energy of a link is known from other data (e.g. thermochemical), certain photoprocesses, in particular spectral regions, may be provisionally ruled out as requiring too much energy, and the number of possibilities to be considered reduced in number. Another difficulty is that the presence or absence of rotational structure in the spectrum is not a rigid criterion of 'predissociation'. For example, sulphur dioxide shows a pressure sensitive blurring of rotation structure at an energy value less than that required to dissociate the molecule into $\text{SO} + \text{O}$. This has been explained as the close approach of two potential energy surfaces, between which transitions are induced by collisions. Wave-mechanics predicts a broadening of rotation levels under these conditions, simulating 'predissociation'. In some circumstances, then, diffuseness does not indicate actual dissociation. It also appears that a fine structured spectrum may occur *with* primary dissociation (independent of collisions), if the delay between absorption and decomposition is longer than a rotational period. The

formaldehyde molecule has a fine structure spectrum in the long-wave ultra-violet; the spectrum becomes diffuse, and a continuous absorption underlying the diffuse region obscures all structure at still shorter wave-lengths. There is photochemical evidence that primary dissociation occurs at all wave-lengths absorbed, and the spectrum may be interpreted in terms of different lifetimes of the excited molecule before rearrangement of its energy permits it to decompose. Apparent diffuseness of fine structure may also result in the case of complex molecules from the overlapping of the great number of closely spaced lines. The interpretation of experimental data is often uncertain or impossible from these causes.

We now attempt to picture the *electronic changes* of molecules by extending the simplified concepts of the geometry of orbitals or 'vibrations' representing electrons given earlier for atoms. Fig. 25 shows how we can in imagination pass from electronic levels of an atom to the levels of a diatomic molecule. At the top left of the diagram an ionized helium atom He^+ is represented with its electron in a $1s$ level. (The symbols $+$ and $-$ there refer to alternate phases of the 'vibration' or wave-function ψ .) We now imagine the helium nucleus split into two halves separated by about 0.75 \AA . The system changes from one of spherical to one of cylindrical symmetry. A *molecular axis* between the two nuclei is produced, and we obtain an ionized molecule of deuterium, D_2^+ , two nuclei united by a single electron. The wave-function representing the electron will obviously change from a spherical to a plum-shaped distribution having rotational symmetry about the axis. This type of orbital is designated 1σ , and any orbital similarly derived from any s electron as a σ_g orbital. Spectroscopically the level is classified as $^2\Sigma_g^+$, the Greek letter replacing the Roman s for atoms, the state being a doublet (because of the 'spin' of the single electron), and the symbols $+$ and g indicating that the

wave-function is unchanged in sign on reflection about a plane containing the molecular axis or by reflection across the midpoint of the axis respectively (opposites are $-$ and u). Now the same molecule D_2^+ can be imagined to be formed by the close approach of a D, 1s atom to a D^+ ion. Since the 'vibrations' will be identical if the electron associates itself with either nucleus, 'resonance' must occur and a new 'vibration' created appropriate to the double system. In the diagram this is denoted $\sigma_g 1s$ and shows the orbital passing to and fro between the nuclei without changing phase. It thus appears that there are two equivalent methods of 'constructing' diatomic molecular orbitals. One is to treat the 'vibrations' as a two-centre problem; this is the most direct for qualitative considerations, but is impossibly difficult mathematically. The other is to approximate to the molecular orbital by suitably combining atomic orbitals. The *atomic* orbitals of the hydrogen atom (those of deuterium are of course practically identical) can be precisely evaluated. By making an allowance for differences of nuclear charge these orbitals may be utilized for heavier atoms with a fair degree of accuracy. At least such an extension will not be wildly inaccurate. It then remains to discover 'how' to combine the atomic orbitals. The methods and difficulties of this are discussed below.

Fig. 25 also shows other molecular levels. 'Vibrations' can interact out of phase as well as in phase. A deuterium 1s atom and a deuterium ion can interact in such a way that the electron changes its 'vibration phase' as it 'resonates' between the two nuclei. Such is termed a $\sigma_u 1s$ orbital; it proves to be *antibonding* or repulsional instead of *bonding* like the σ_g orbital. This repulsive state of the D_2^+ molecule is spectroscopically designated $^2\Sigma_u^+$. If the nuclei are imagined to collapse together to give a He^+ ion, the latter will have a $2p$ electron, so that the electron in the molecular level may also be termed $2p\sigma$.

The nucleus of the $\text{He}^+ 2p$ can also be imagined to be split in a different direction so that the two nuclei lie in the nodal plane instead of on each side of it. This process generates a different molecular level with the electron in a $2p\pi$ orbital.

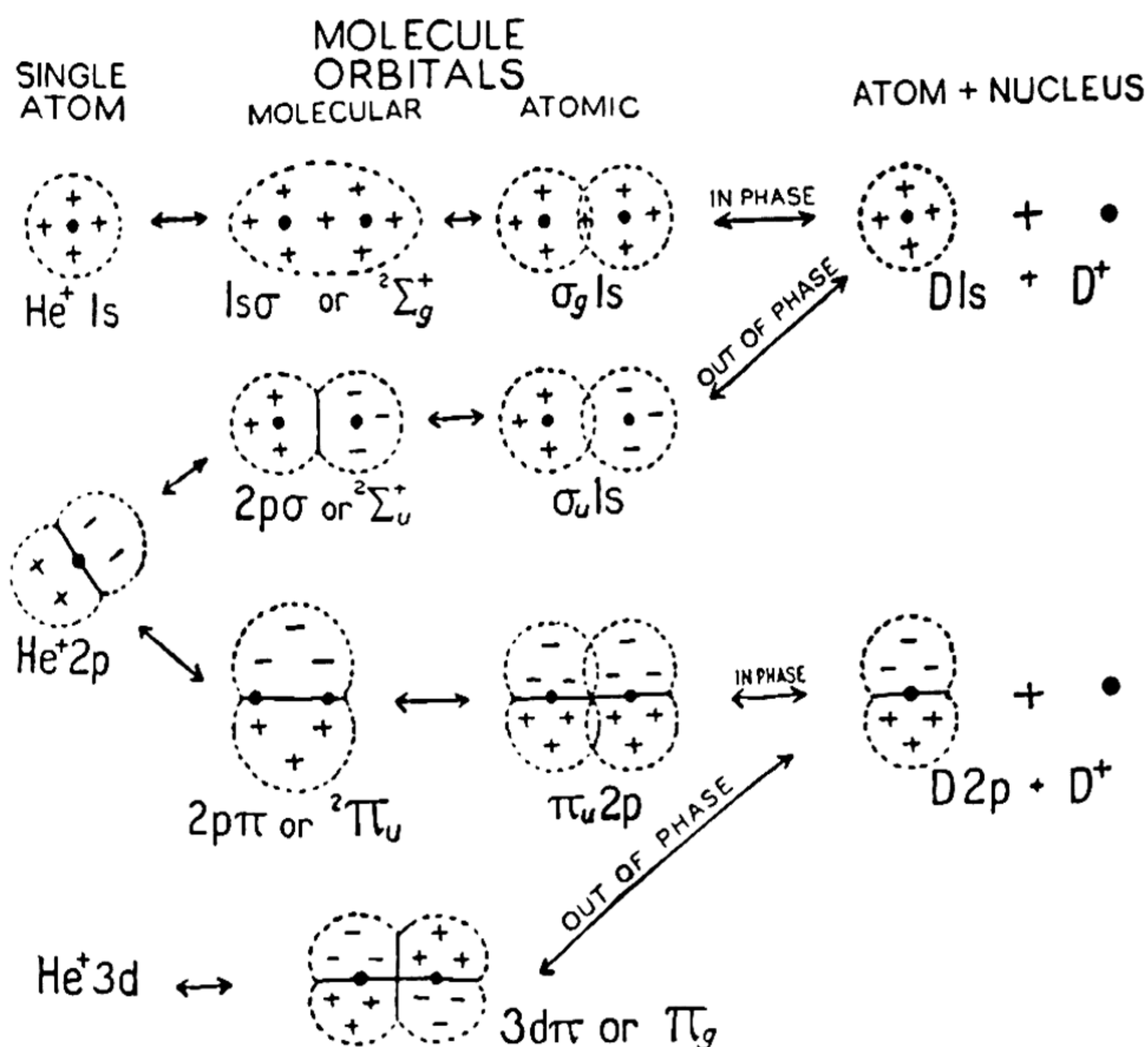


FIG. 25. Alternative ways of constructing orbitals of diatomic molecules. (Symbols + and - refer to alternate phases of the wave and not to electric charges.)

This same level, also termed π_u , may be reached by coupling a $D 2p$ atom with a D^+ ion. A $D 2p$ atom can also couple with a D^+ ion in three other ways: firstly to give a π_g electron (or $3d\pi$) with two nodal planes at right angles, containing the molecular axis and normal to it respectively, and secondly in two other ways of σ_g or σ_u type. These are shown with diagrammatical wave-forms in the figure. The main conclusions from the above analysis are that molecular levels are

related to atomic levels, and that four chief types of diatomic molecular orbitals are distinguishable: σ_g , plum-shaped with axis along the chemical link; σ_u , antibonding with a nodal plane normal to the molecular axis (i.e. the electron avoids the centre of the molecule); π_u , bonding (less than σ_g), with a nodal plane containing the molecular axis, shaped like a double bun; and π_g , antibonding, like a combination of σ_u and π_u .

The molecule considered above, D_2^+ (the same considerations apply to H_2^+), is unusual in having only one electron to bind the nuclei together, which it does when the wave-functions resonating between the nuclei have the same phase on the two sides. A strong link can be formed in this way only when the two atoms in the molecule are identical, for only then is the 'resonance' possible in large measure. The normal covalent chemical link has a *pair* of electrons, of opposite spin, in the bonding orbital. Two 1s hydrogen atoms can interact so that both electrons, spin paired and in phase with one another, form a σ_g orbital. This represents the normal H_2 molecule, spectroscopically classified as $^1\Sigma_g^+$ (singlet state since there are *two* electrons). The interaction liberates energy, and the energy-distance curve for the atoms shows a deep minimum corresponding to stable molecule formation (Fig. 26).

The atoms can also interact with their electrons out of phase and not spin-paired, so producing a new level $^3\Sigma_u^+$ with one electron entering a σ_g molecular orbital and the other a σ_u . This interaction is partly bonding and partly antibonding; in fact the latter predominates and the energy-distance curve shows no minimum. The molecular level is not fictitious, however, for the continuous spectrum in the ultra-violet obtainable from H_2 , and important as a light source, arises from transitions from a higher molecular level to this one. (See Figs. 20 and 27.)

The simple mechanical analogy of the coupling of two

atomic orbitals in phase to give a σ_g molecular orbital does not explain why the molecule is more stable than the separate atoms, i.e. why firm chemical linking with evolution of energy occurs. The chief part of the energy liberated when hydrogen atoms combine to the molecule is called 'resonance'

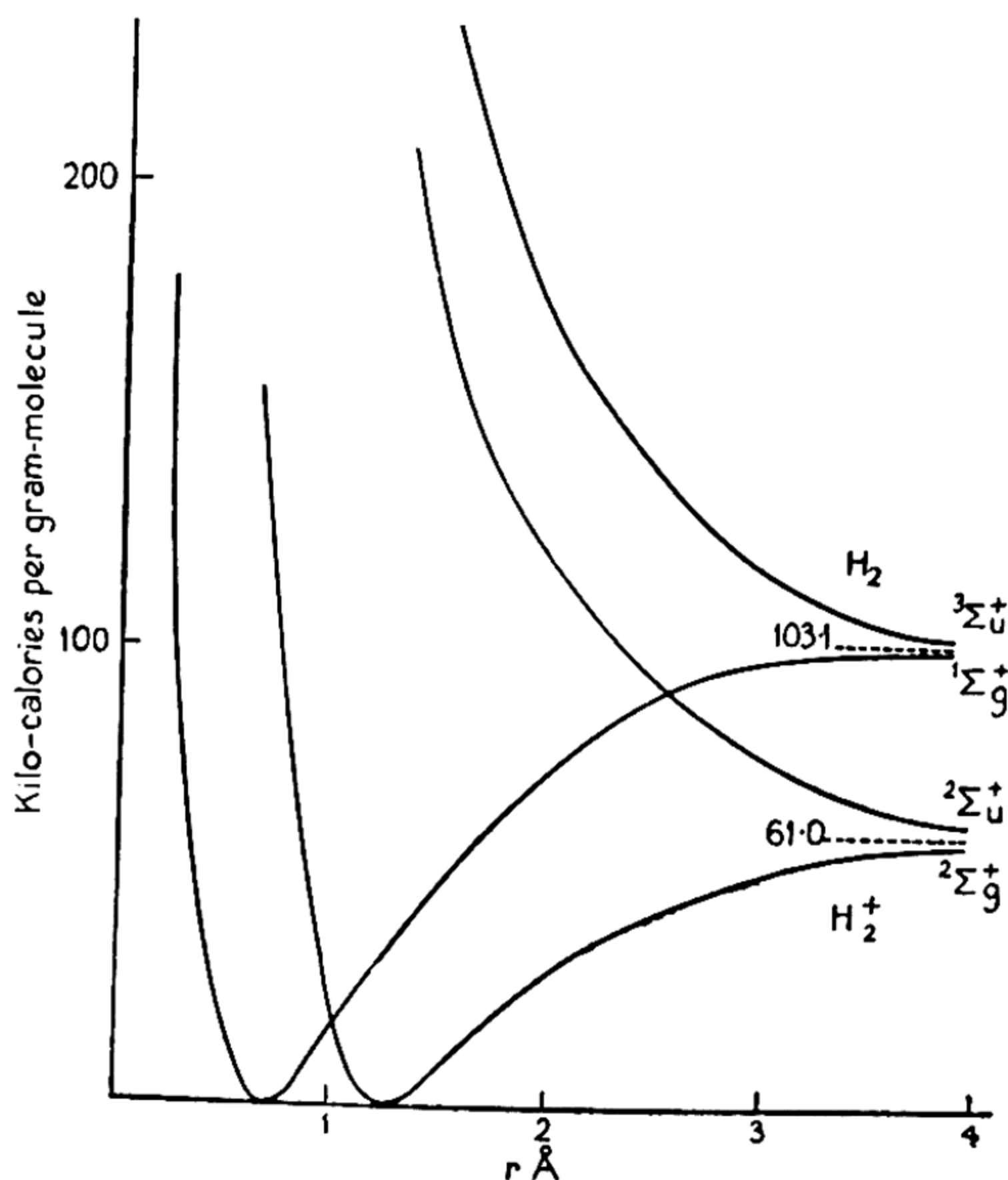
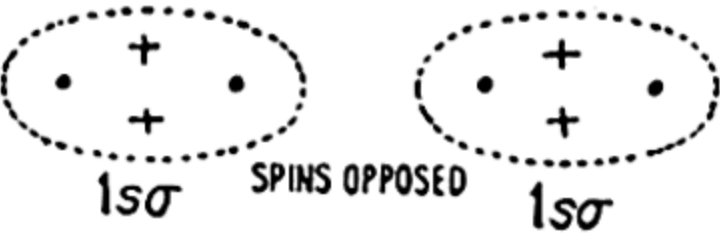

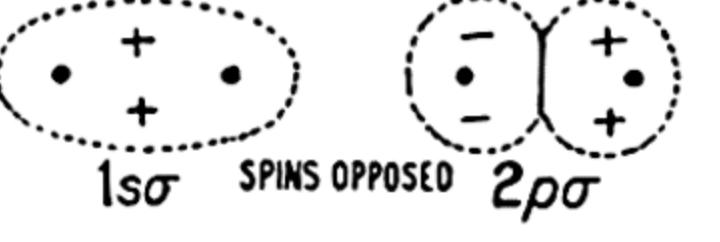

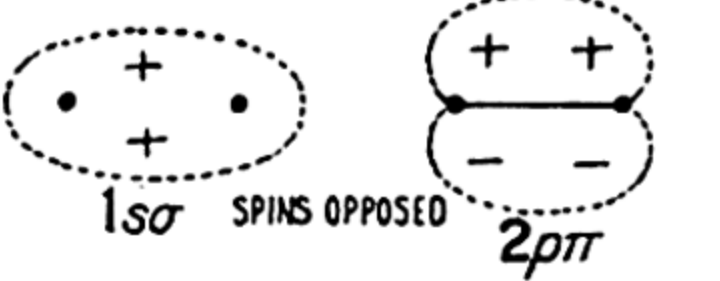
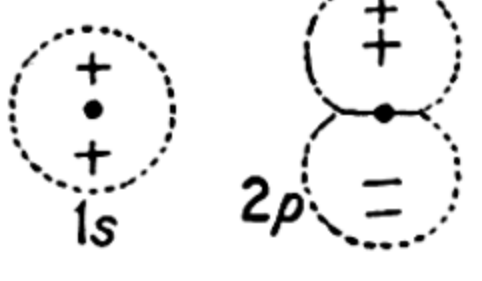
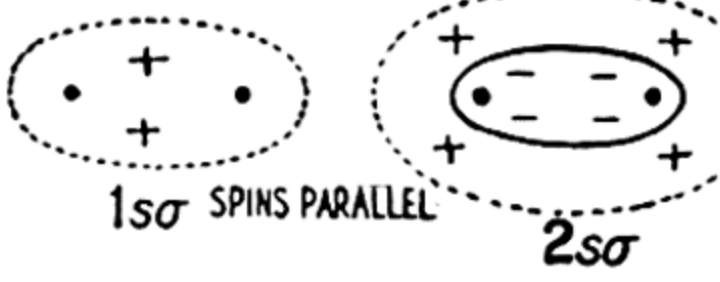
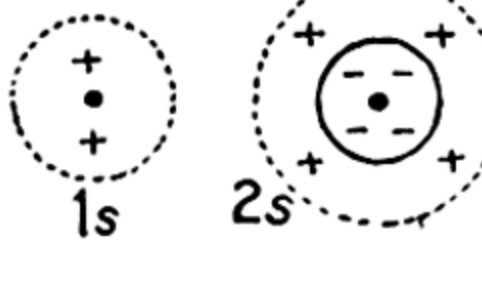
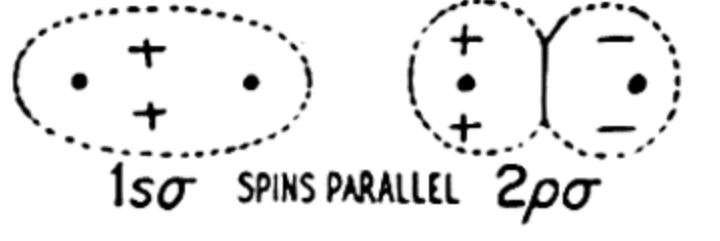



FIG. 26

energy, since one way of picturing the molecule it to regard the electrons as 'changing nuclei' through the overlap of their orbitals. The energy evolution may be regarded as a consequence of the Uncertainty Principle. The electron in a single H atom in its ground state must have a momentum corresponding to the accuracy with which the position is defined, though its value is taken as the zero for ordinary estimates of the momentum of the higher states. This ground state momentum means a certain energy of the electrons.

When two H atoms approach one another having electrons with anti-parallel spins they can interchange orbits and the space in which each electron moves is about twice as great.

STATE SYMBOL (see preceding figure)	MOLECULAR ORBITALS OF ELECTRONS 1 AND 2	ATOMIC ORBITALS OF PRODUCTS OF DISSOCIATION
${}^1\Sigma_g^+$		
${}^1\Sigma_u^+$		
${}^1\Pi_u$		
${}^3\Sigma_g^+$		
${}^3\Sigma_u^+$		

LOWER ELECTRONIC LEVELS OF H_2

FIG. 27

This reduces the uncertainty of the momentum so that the combined system of two atoms has a lower 'electronic zero point energy' than that of the two atoms separated from each other, i.e. energy is liberated when they combine.

The solution of the energy levels of the systems H_2^+ and H_2 , i.e. of one or two electrons moving in the field of two nuclei, making use of the Schrödinger equation, is one requiring very laborious calculation. For other molecules this

fundamental method cannot be directly employed. The electrons move in the fields of the various nuclei, and the expression for the potential energy V is complicated so that the mathematics of the differential equation become intractable. By means of varying degrees of approximation, however, useful results can be obtained. There is more than one way of making progress, the details of which need expert acquaintance with the subject. The basic principles and simplifying assumptions are as follows. The valency electrons of the atoms forming the molecule are expressed by hydrogen-like atomic wave-functions, assuming a simple Coulomb form for V and using Schrödinger's equation. Next it is assumed that the orbitals so obtained for the electrons are not seriously distorted in the neighbourhood of the atoms in the process of molecule formation. An approximate molecular orbital is then constructed by combining the atomic orbitals. Two methods are available for this. In the homopolar method, as applied to a molecule such as H_2 , the molecular wave-function is written as $(\psi_{A1}\psi_{B2} + \psi_{A2}\psi_{B1})$, where ψ_{A1} is the atomic wave-function for electron 1 on nucleus A , ψ_{B2} is for electron 2 on nucleus B , etc. In the molecular orbital method the molecular wave-function is treated as a linear combination of atomic orbitals, e.g.

$$\begin{aligned}
 &(\psi_{A1} + \psi_{B1})(\psi_{A2} + \psi_{B2}) \\
 &= \psi_{A1}\psi_{A2} + \psi_{B1}\psi_{B2} + (\psi_{A1}\psi_{B2} + \psi_{A2}\psi_{B1}).
 \end{aligned}$$

This differs from the first treatment by the first two terms, which refer to *both* electrons being on one nucleus, i.e. to the possibility of the molecule passing through ionic phases H^+H^- . The homopolar method makes no allowance for both electrons sometimes being near one nucleus of the molecule in the ground level of H_2 , while the molecular orbital method overemphasizes the importance of this electronic arrangement, so that the two methods bracket the truth. The difference between the ground level of the H_2 molecule, $^1\Sigma_g^+$ ($2\sigma_g$

electrons, spin-paired) and the next singlet level $^1\Sigma_u^+$ (1 σ_g and 1 σ_u electron, spin-paired; σ_g given by *sum* of atomic orbitals, σ_u by their *difference*) appears as the transfer of charge $H_2 \rightarrow H^+H^-$ by the homopolar treatment, while by the molecular orbital method it is a $\sigma_g \rightarrow \sigma_u$ orbital change, i.e. the transfer of an electron from a bonding to an antibonding orbital. As with all attempts to reduce wave-mechanics to simple pictorial form, it is not easy to see the connexion between these two partial statements of the truth.

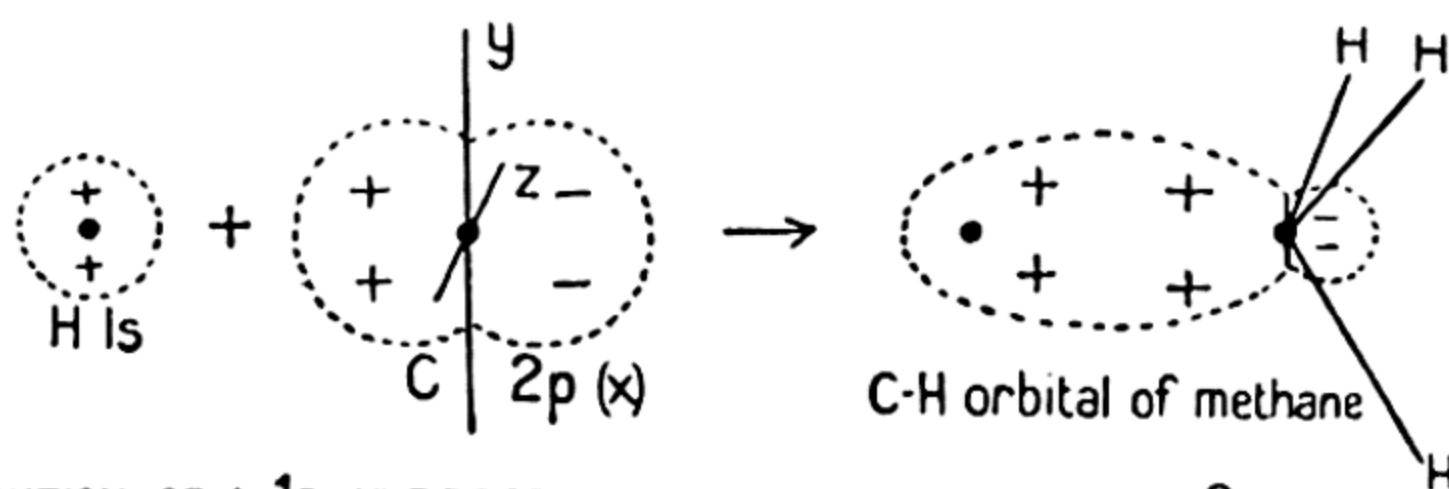
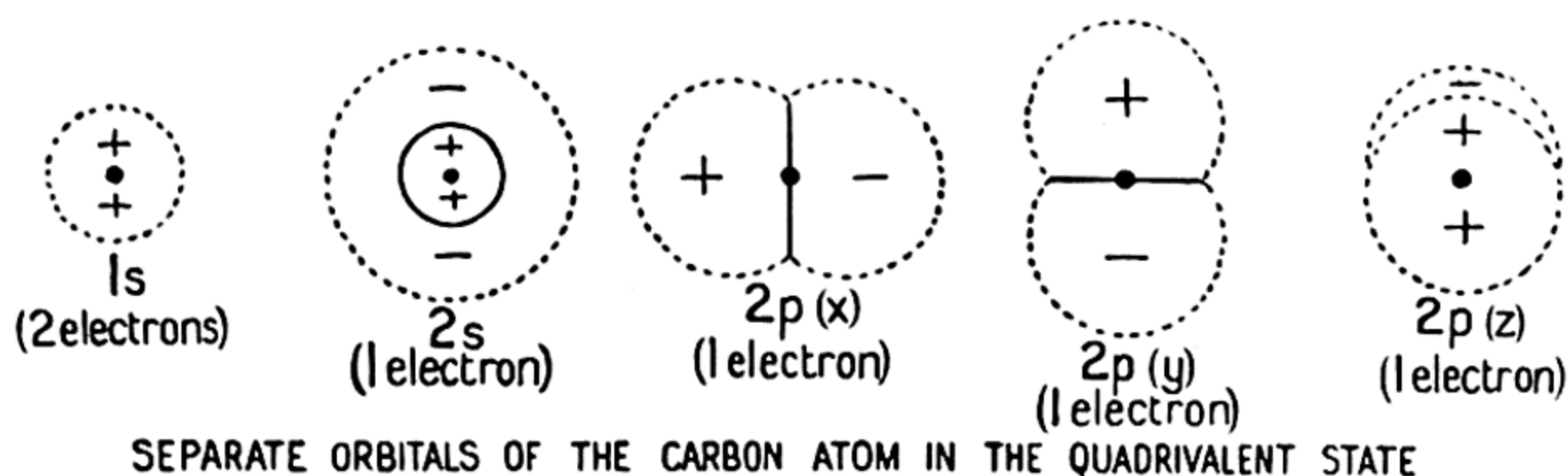
In extending the wave concepts of orbitals to other molecules than H_2 it is convenient to fix attention again on the 'geometry' of the system, i.e. the arrangement of the wave forms in space. As explained above, for diatomic molecules we have the following orbitals; σ_g which may be regarded as two atomic s orbitals combined in phase, σ_u as combined out of phase, while π_u and π_g correspond to atomic p orbitals combined in and out of phase respectively. The molecular *state* is classified according to the *resultant* symmetry of all the orbitals, and is denoted by Greek capital letters. If the resultant has rotational symmetry about the axis, as have σ orbitals and also a right-angled combination of π orbitals, the level is denoted as Σ . Levels of diatomic molecules of lesser symmetry corresponding to atomic P and D states are classified as π and Δ . Some of these atomic and molecular orbital types are depicted in Figs. 20 and 27.

The problem of the nature of carbon-carbon linkages is important because of the interest in colour in organic compounds. The carbon atom has six electrons. The lowest atomic orbital, $1s$, contains two electrons. The remaining four electrons are distributed between the next higher orbitals, a $2s$ and the three mutually perpendicular $2p$ orbitals, in accordance with the Pauli principle (0, 1, or at most 2 (spin-paired) in any orbital). The configuration of lowest energy is $1s^2 2s^2 2p^2$, but owing to the different possibilities of arrangement of the two p electrons in the three p

orbitals and the effects of electron spin there are three separate atomic states of this configuration. The lowest, and therefore the ground state of the carbon atom, is a 3P state; the superscript 3 (read as triplet) indicating the number of electrons of unpaired spin $+1$. In this state the two $2s$ electrons are spin-paired, but the two $2p$ electrons occupy separate orbitals with spins parallel. A higher atomic state is 1D , the superscript 1 (singlet) showing that all spins are paired; the two $2p$ electrons again occupy separate orbitals. The third state is 1S where all spins are paired and the two $2p$ electrons occupy one orbital (the S symmetry arising from the fact that they may be imagined to occupy all the $2p$ orbitals in turn). A 'divalent' carbon atom roughly corresponds to the 3P state; a truly chemically divalent atom should, however, have the two p electrons with *independent* spins, and this can be conceived of only as a combination of the 3P and 1D states. A 'quadrivalent' carbon atom needs excitation of the atom to a new configuration $1s^2 2s 2p^3$; one electron in the $2s$ and three in the $2p$ orbitals. Here six atomic states are derivable from the several combinations of occupied orbitals and electron spins. As in these states the spins are always either paired or parallel, the 'chemically quadrivalent' atom with four electrons with *independent* spin must be regarded statistically as a suitable combination of atomic states.

Disregarding the finer matters connected with electron spin we may picture the quadrivalent carbon atom as having a spherical distribution of electron density which can be hypothetically resolved into spherical s orbitals and three mutually perpendicular hour-glass shaped p orbitals (Fig. 28). If we imagine this atom combining with four $1s$ hydrogen atoms to give CH_4 , we must take account of the characteristics of the wave-motion assumed for the behaviour of electrons. The combination of an s electron with a p electron will produce a 'hybrid' type of bond (see Fig. 28). It would be naïve, however, to assume that the final molecule CH_4 should have

three such C—H links at right angles and a fourth C—H link derived from s electrons only, both because of the vibrations coupled to each other merging into new vibrations and because the p orbitals conceived of above have merely *arbitrary* rectangular axes which cannot define *real* C—H directions. The greatest strength of bonding may plausibly be



COMBINATION OF A $1s$ HYDROGEN ELECTRON ORBITAL WITH A $2p$ CARBON ELECTRON ORBITAL TO GIVE A 'HYBRID' C-H MOLECULAR ORBITAL OF MAINLY σ_g CHARACTER
(+ and - symbols refer to opposite phases of the electron waves)

FIG. 28

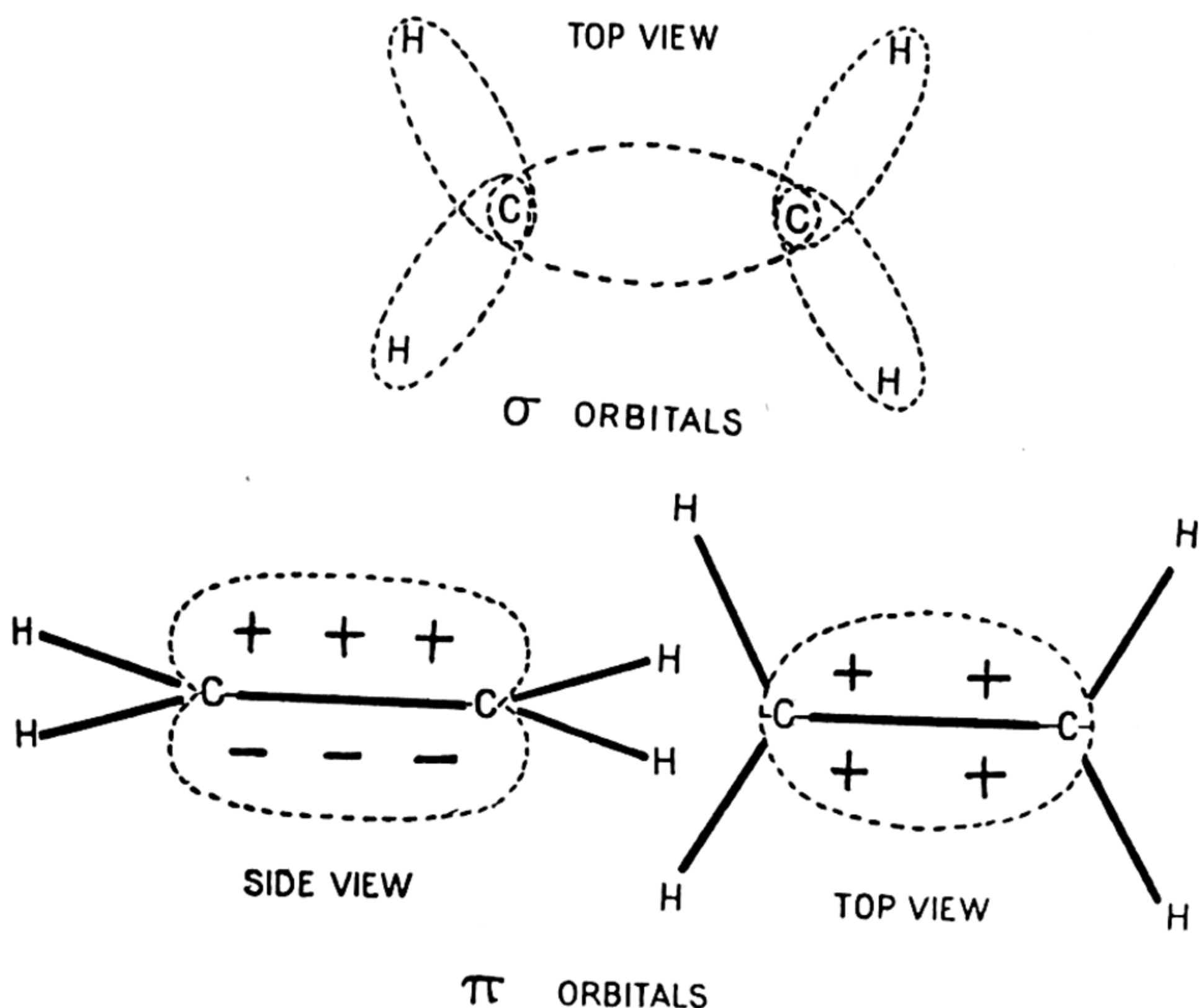
expected when the atomic orbitals mutually adjust themselves to give the maximum overlapping in phase. This occurs with a tetrahedral arrangement of four equal bonds because here the vestigial 'tails' of opposite phase derived from the p electrons are reduced to a minimum size. Such bonds have axial symmetry and are mainly σ_g in character; the vestigial tail representing a little σ_u admixture. All single C—H links as in methane or C—C links as in ethane or diamond rather closely resemble the H—H link because of their mainly σ_g

character; their light absorption, for example, lies in the far ultra-violet because of the high energy necessary to excite one electron of the link to the next higher molecular orbital (of σ_u character).

In graphite we find a somewhat different type of carbon link. Here there are three equal C—C bonds of σ_g character at 120° to each other in a plane while a fourth bond is much weaker and is directed both ways at right angles to the plane. To understand this disposition we may picture the formation of the radical CH_3 from three H atoms and a quadrivalent C atom. One p electron of the latter will be unused and left in a largely unaltered hour-glass shaped orbital. Hybrid bonding with mutual adjustments must occur in forming the three C—H links. The maximum overlapping is obtained when three equal hybrid bonds are formed at 120° in the nodal plane of the unused p orbital; this being facilitated by the fact that only two p electrons hybridize with the s electron of the carbon instead of three as in CH_4 , so that the 'vestigial tail' of opposite phase is smaller. The peculiar fourth valency of graphite is a metallic linkage arising from the p electrons whose axis is at right angles to the C—C linkages.

These considerations lead to the idea that the 'double bond' of organic chemistry is not the equivalent of two 'single bonds', but rather is based on the above 'trigonal' arrangement of valency links. In ethylene, for example, there is a 'single bond' skeleton of C—H and C—C links of essentially σ_g character all in a plane and at 120° to each other. The extra link of the double bond may be visualized as a π_u orbital obtained by interaction in phase of atomic p orbitals of the carbon atoms (Fig. 29). As the p orbitals are hour-glass shaped with a nodal plane in the plane of the single links, the π_u orbital will be shaped somewhat like a bun split across into two halves by the same nodal plane. A 'double bond' is then regarded as a combination of one σ_g type

molecular orbital and one π_u orbital. Since these do not overlap much, because the nodal plane of the latter passes through the former orbitals, it is permissible as an approximation to neglect their interactions. The energy difference between the



ETHYLENE

FIG. 29

molecular levels of ethylene is then roughly calculable from fundamental constants on the following lines. We disregard all the 'single' bonds in the molecule and imagine the two carbon atoms placed at the right distance apart in the molecule, each atom having an electron in a $2p$ orbital, the two nodal planes being the same. The atomic orbitals are numerically approximated to by using the Schrödinger equation as

for hydrogen, using a suitable value for the 'apparent nuclear charge' of the carbon to allow to some extent for the influence of the other electrons. Molecular orbitals are constructed as already described by combining these atomic orbitals. In the ground state both electrons are in a π_u orbital (two $2p$ orbitals in phase). In the excited state one electron remains in the π_u orbital while the other is raised to a π_g orbital, the latter having an extra nodal plane at right angles to the molecular axis, and corresponding to out-of-phase interchange of the p orbital of that electron as it 'passes' from one atom to the other. Calculation of the energy difference of these molecular orbitals yields a value of 170 k. cal. per mole, corresponding to a wave-length of 1,670 Å. Ethylene actually absorbs at 1,750 Å. The effect of light absorption at 1,750 Å on ethylene is to produce a new nodal surface at right angles to the C—C π orbital, i.e. to make one of the π electrons 'antibonding' (out-of-phase relationship). Since in any orbital change, such as $s \longleftrightarrow p$ for an atom, light must be polarized with electric vector at right angles to the new nodal plane developed, we deduce that, for strong absorption to occur, the electric vector of the light must lie along the C—C link of ethylene. (Cf. Figs. 17 and 30.)

Excitation of the σ bonds in ethylene requires much more energy. Single-bonded molecules with σ bonds only absorb in the far ultra-violet, e.g. methane at 1,200 Å and ethane at 1,400 Å. Absorption of light in the longer-wave ultra-violet and the visible region is confined (in organic chemistry) to double-bonded molecules, becoming stronger and longer if chains of alternate double and single bonds ('conjugation') are present. From the point of view of the theory of 'colour', therefore, the extension of wave-mechanical ideas to conjugated molecules is of interest. The simplest example is butadiene. We focus attention only on the π orbitals. Starting with the four carbon atoms in the chain, each with one electron in a $2p$ orbital with nodal plane at right angles to the

page, we can imagine the atomic orbitals to overlap to give molecular orbitals in a number of ways. One orbital corresponds to overlapping in phase of all four $2p$ orbitals (1, Fig. 31). Two electrons may be assigned to fill this orbital.

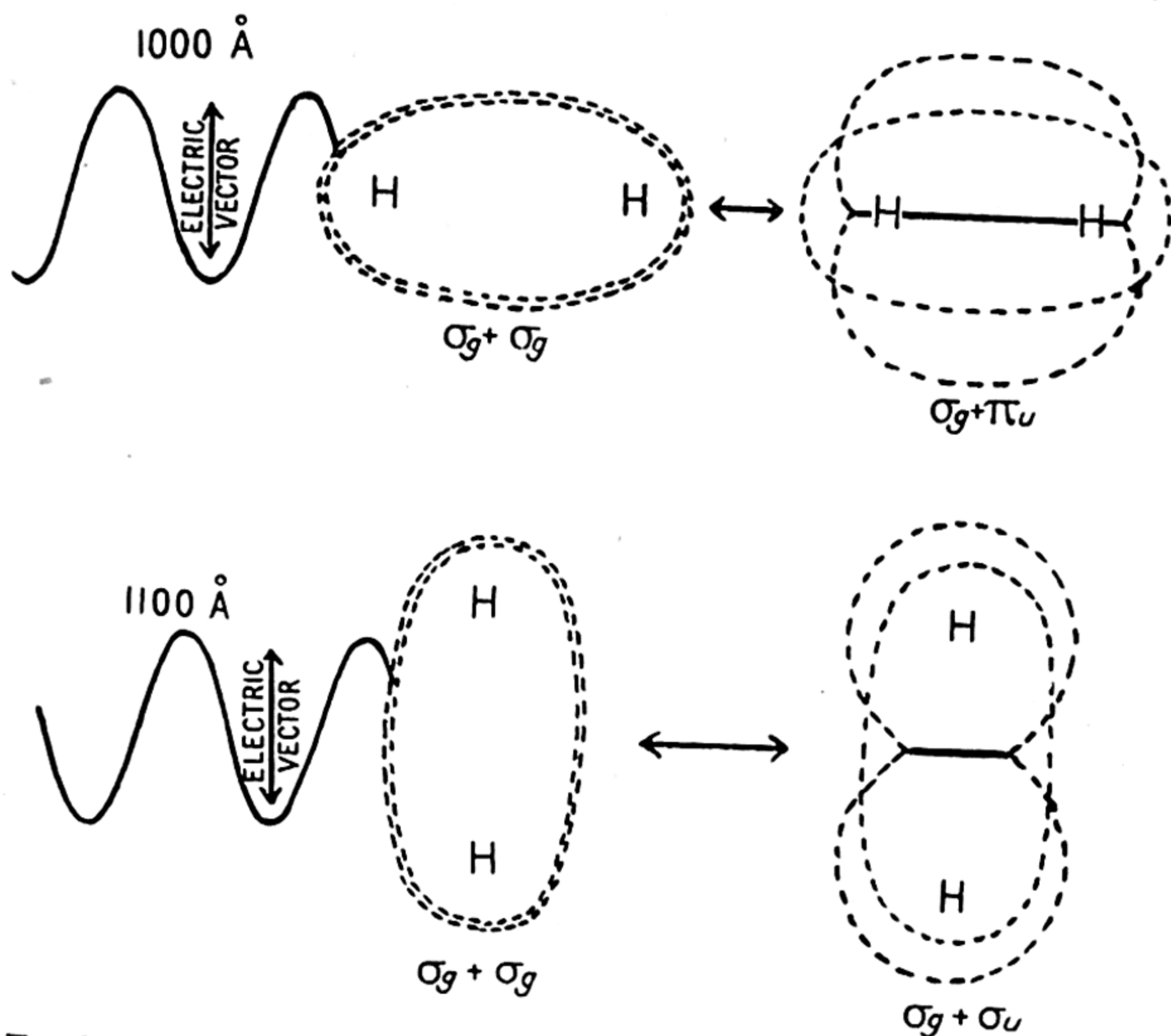
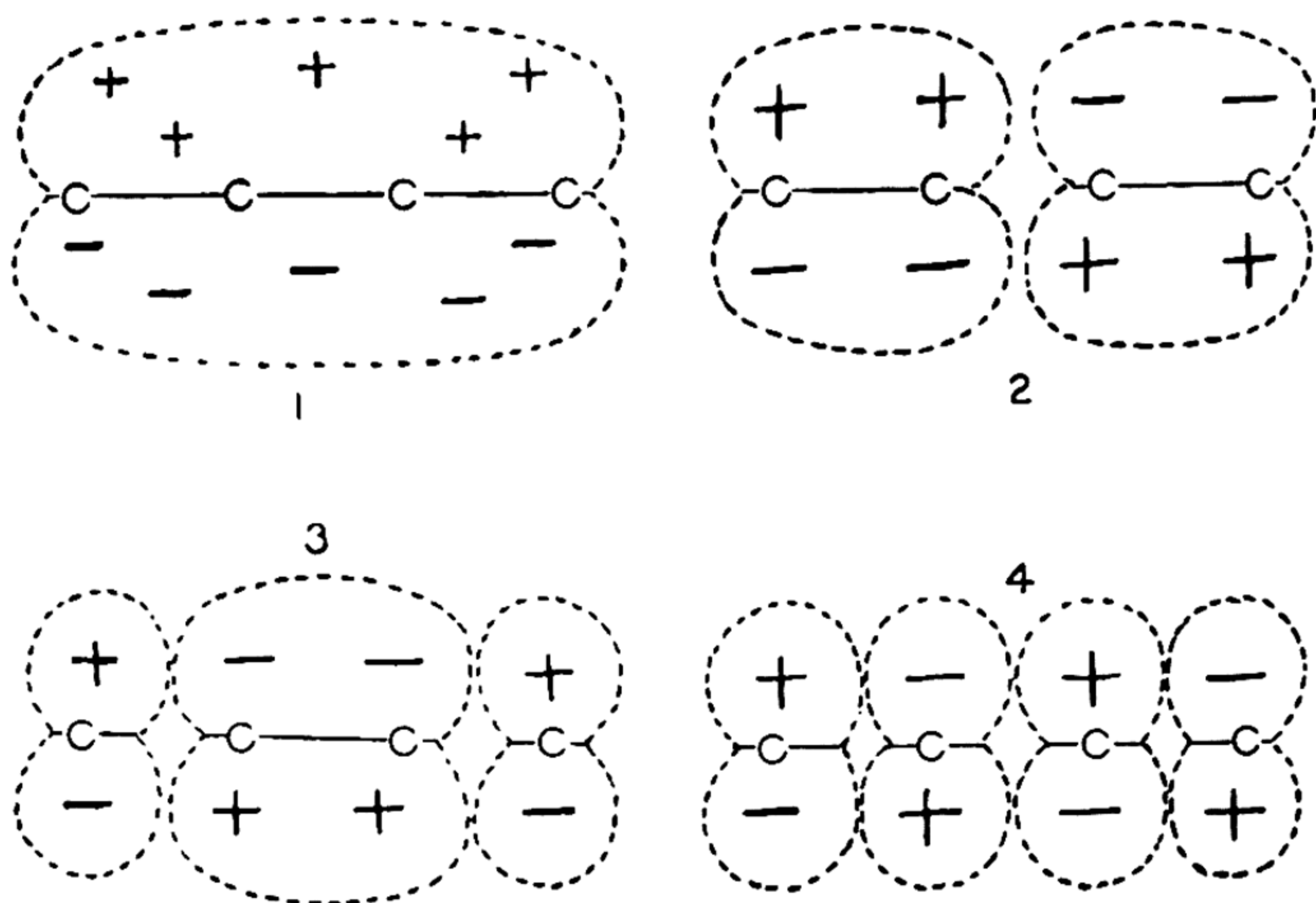


FIG. 30. Absorption or emission of light by a hydrogen molecule. One electron moves on absorption of light to a higher orbital with a nodal plane at right angles to the electric vector.

The next orbital has a second nodal plane at right angles to the centre of the middle C—C link (2, Fig. 31). If two electrons are allotted to this orbital we obtain the ground level of the molecule as the resultant of these orbitals. Other higher orbitals (3 and 4, Fig. 31) with two and three additional nodal planes take an electron from one of the lower orbitals when the molecule is excited by absorption of light. Four transitions, corresponding to four absorption bands, are clearly possible. The molecule is zigzag but planar and can assume

two forms, extended (*trans*), and bent back (*cis*). These have different absorption intensities for the different transitions. The observed longest-wave absorption band is at 2,100 Å. The same principles are applicable to longer conjugated



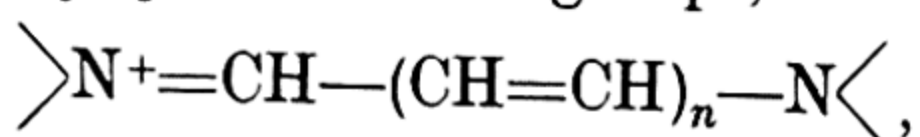
MOLECULAR ORBITALS OF THE π ELECTRONS
OF BUTADIENE $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$

FIG. 31

chains. We may regard the chain as a set of vibrators coupled together; the mechanical equations giving the resultant frequencies of the whole chain in terms of the properties of the individual vibrator units are very similar to the wave-mechanical equations which give the energies of the molecular orbitals in terms of the properties of the atomic orbitals. β -carotene, for example, has 22 carbon atoms in a conjugated chain. It therefore has 11 molecular orbitals of its π electrons filled in the ground state. Absorption of blue light excites one electron from the 11th orbital (one nodal plane along chain and 10 trans-axial nodal planes) to the 12th, developing an

extra trans-axial node. With increasing length of chain the number of possible transitions increases, owing to the larger number of filled orbitals in the ground state from which an electron can be excited, and the wave-length corresponding to the transition of least energy increases, since the transitions between neighbouring orbitals decrease in energy the higher those orbitals are. The treatment is complicated by the many stereochemical forms of the planar chains. We are able, however, to see why increasing conjugation causes absorption to move to longer wave-lengths and to become more intense, and to estimate the actual position of absorption bands in the simpler cases. (See Fig. 32.)

For structures of the butadiene type the problem of obtaining molecular orbitals from atomic orbitals resembles that of finding the stationary waves possible in a uniform chain of fixed length. Molecules such as $R_1-(CH=CH)_n-R_2$, where R_1 and R_2 are C_6H_5- or similar groups,



cyanine and related dyes with end-groups, make the problem one analogous to that of finding the possible stationary waves in a chain with end lengths of different thicknesses, equal to each other or unequal according as the molecule is symmetrical or unsymmetrical. Here the complexity of the problem makes it difficult to do more than to compare the variation of the longest absorbed wave-lengths, calculated and observed, with the number of atoms in the chain. Studies of this kind are of assistance to the chemist trying to understand his phenomena and to the wave-mechanician who seeks for guidance in permissible simplifications of theory. Two opposite aspects of the problem have to be balanced against each other; simplification of the mathematical treatment to make quantitative calculations possible at all, and elaboration of the above idealized theory to allow for interactions between the molecular wave-forms assumed. Advance

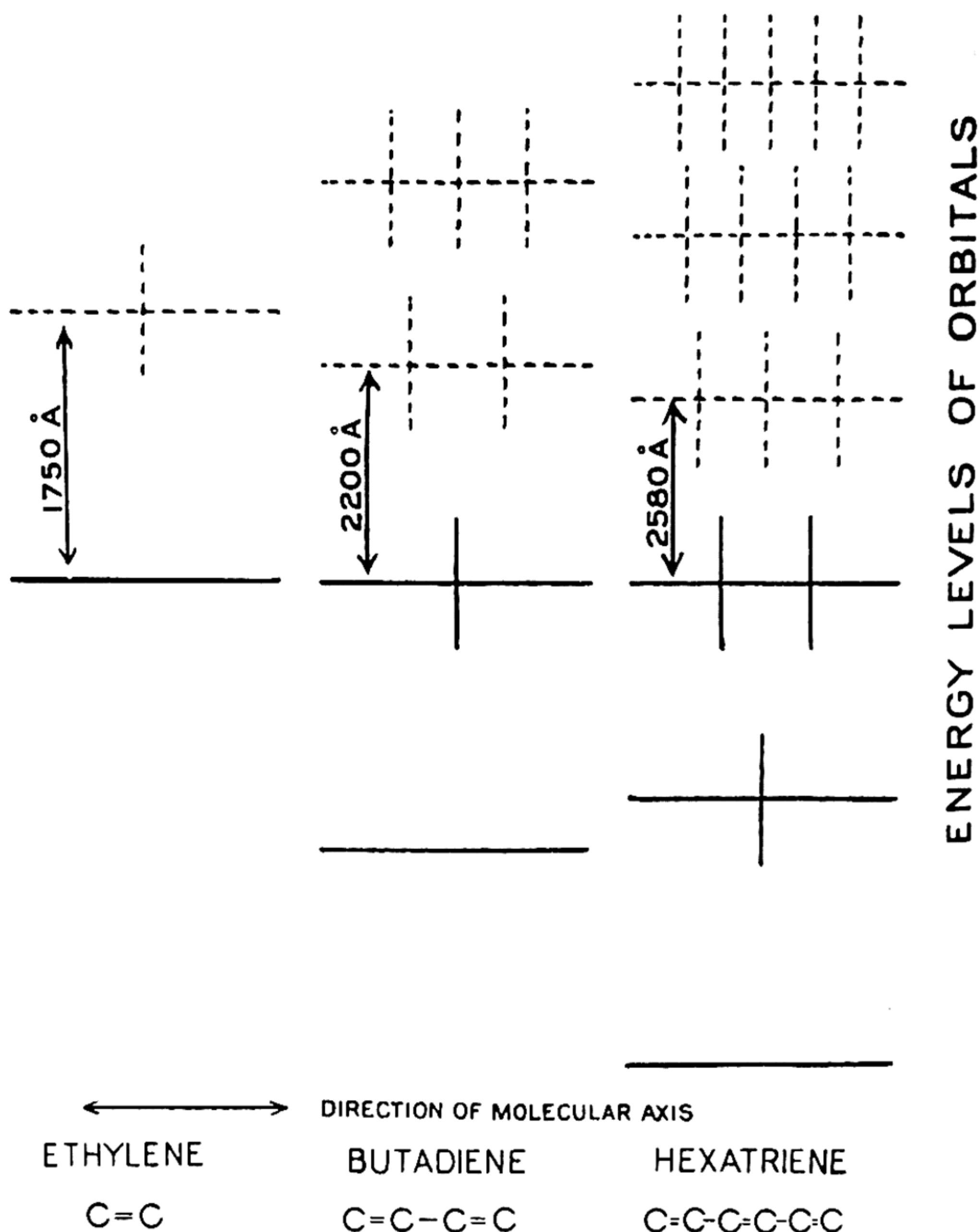
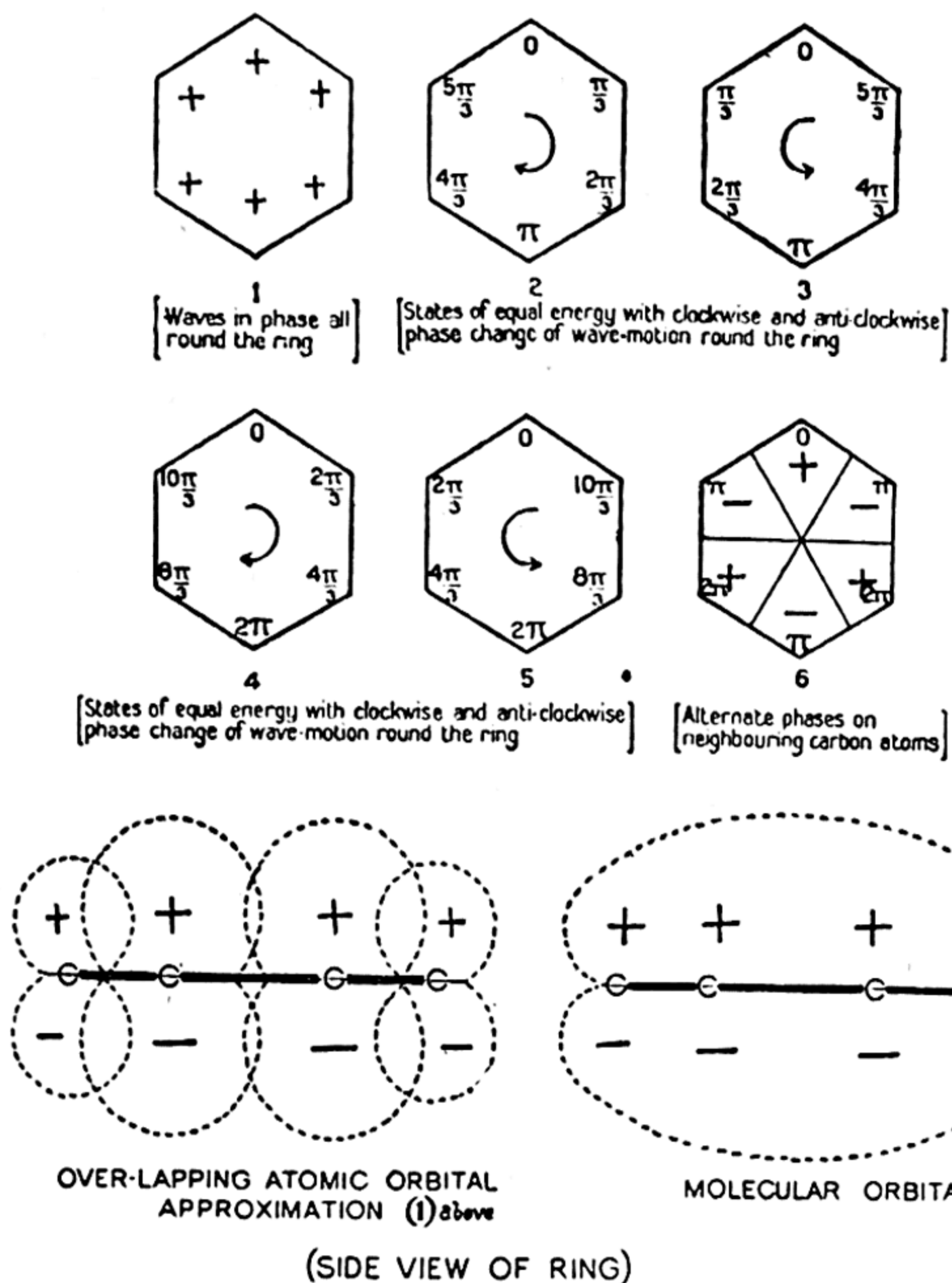


FIG. 32. π molecular orbitals of conjugated polyenes. Orbitals represented by their nodes, which form surfaces at right angles to the paper. Orbitals filled in the ground state shown with full lines; unfilled higher orbitals by dotted lines. Longest wave-length of absorption shown by double arrows indicating transition of one electron. Molecular axis zigzag but planar through interaction of the π electrons.

here is therefore bound to be slow and tentative in character.

The benzene molecule is one obviously capable of treat-



π ORBITALS OF BENZENE

FIG. 33

ment along these lines. The individual orbitals are shown in Fig. 33. We start with six carbon atoms in a plane hexagon, each atom having one $2p$ electron. The six lowest molecular orbitals are as shown. In the first all the $2p$ orbitals are in phase, the common nodal plane of the orbitals and of the resultant molecular orbital being that of the ring. The second

and third correspond to 'wrapping a wave' round the ring, so that each successive carbon atom orbital is $\pi/3$ out of phase; the two orbitals corresponding to clockwise and anti-clockwise rotations of the wave round the ring. The fourth and fifth orbitals are derived by 'wrapping' two complete waves round the ring, and the sixth from three waves, i.e. alternate phases on each atom. In the ground level the six 'aromatic' electrons occupy the three lowest orbitals, and their resultant gives the molecular orbital configuration representing the normal benzene molecule. Absorption of ultra-violet light causes an electron to pass from orbital 2 or 3 to 4 or 5. Rough quantitative treatment indicates that benzene should absorb about 2,450 Å (actual absorption at 2,600 Å), naphthalene, by similar arguments, about 2,950 Å (exp. 2,750 Å), and anthracene about 3,650 Å (exp. 3,700 Å). When the benzene problem is examined in more detail it can be shown that the orbital change 2 or 3 to 4 or 5 involves several different possibilities, depending on the relative directions of rotation of the orbitals and of the effects of electron spin. These give rise to several separate possible absorption positions in the ultra-violet. The complete wave-functions of the benzene molecule, built up from molecular orbitals obeying the Pauli principle, and themselves made up of linear combinations of $2p$ atomic orbitals of hydrogen type fitted to carbon atoms, are lengthy to evaluate, owing to the complicated integrals involved, but approximate solutions have been obtained. Seven main energy levels are obtained, described as follows in conventional symmetry notation, together with the calculated energies above the ground level: ${}^1A_{1g}$, ground level; ${}^3B_{1u}$, 34.5 k.cal./mol.; 3E_u , 50.5; ${}^3B_{2u}$, 69; ${}^1B_{2u}$, 115; ${}^1B_{1u}$, 133; 1E_u , 184. The quantum-mechanically permitted transition ${}^1A_{1g} \rightarrow {}^1E_u$ is identified with the very strong absorption band of benzene at 1,800 Å (calc. from energy change 184 k.cal./mol., 1,500 Å). The well-known absorption at 2,600 Å agrees with the change ${}^1A_{1g} \rightarrow {}^1B_{2u}$. This band is theoretically

'permitted' only through the cooperation of a certain type of nuclear vibration of E_g^+ symmetry, corresponding to a lengthening and shortening of the hexagonal atomic skeleton along one direction. The strong, temperature insensitive absorption bands arise when the ground state non-vibrating molecule passes by light absorption to the upper excited level, the latter having one quantum of E_g^+ vibration in addition to its electronic energy. Further, since the hexagon expands somewhat on excitation, symmetrical 'breathing frequency' A_{1g} type vibrations are also set up in the nuclear framework by the operation of the Franck-Condon principle (see p. 88). The strong bands therefore show a vibration 'partial band' sequence whose frequency differences give a value for the frequency of the symmetrical A_{1g} atomic vibration of the upper level. Weaker bands, which increase in strength at higher temperatures, arise from transitions from molecules in the lower electronic state already possessing one quantum of the E_g^+ vibration to the upper state with no E_g^+ vibration; A_{1g} vibrations are, however, still excited. These relationships are all shown in Fig. 34, which also shows the transitions involved in the fluorescence spectrum, whose 'partial band' structure gives ground-state vibration frequencies, and the general appearance of the absorption spectrum of benzene as a vapour and in solution. The regular 'partial band' vibrational structure of the absorption bands of other hydrocarbons such as anthracene must also be ascribed to 'breathing frequencies' through the operation of the Franck-Condon principle on absorption. In many polynuclear hydrocarbons and dyes, phthalocyanines, porphyrins, and in chlorophyll and 'visual purple' narrow bands devoid of vibrational structure are observed. This means that the dimensions and hence the linkage force constants are scarcely affected by the excitation of one π electron to a higher orbital, the antibonding effect of the latter being 'spread' over a large number of links.

A peculiar effect known as 'thermochromy' is shown by certain highly conjugated systems. The substance changes its colour by acquiring new bands as the temperature is

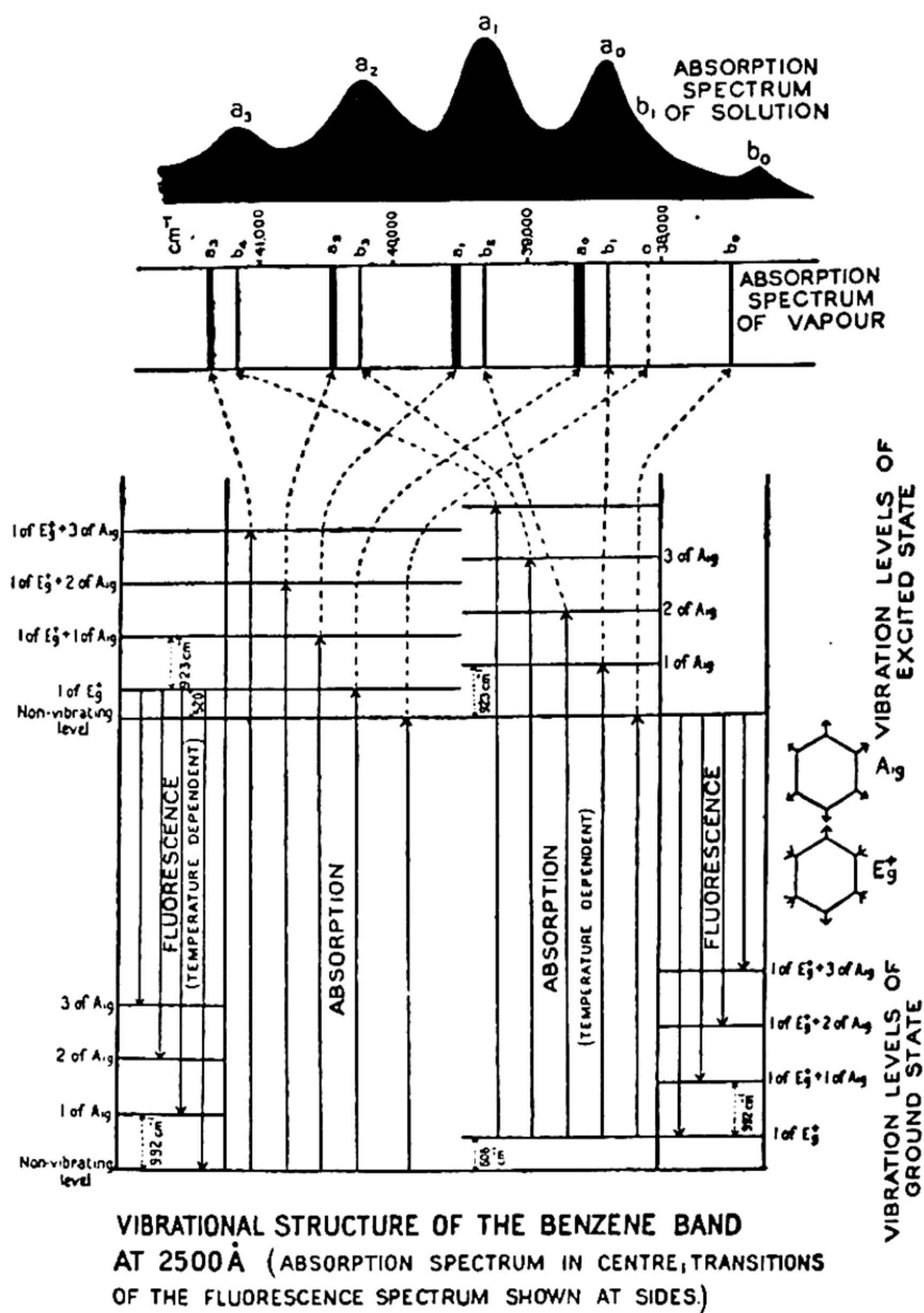
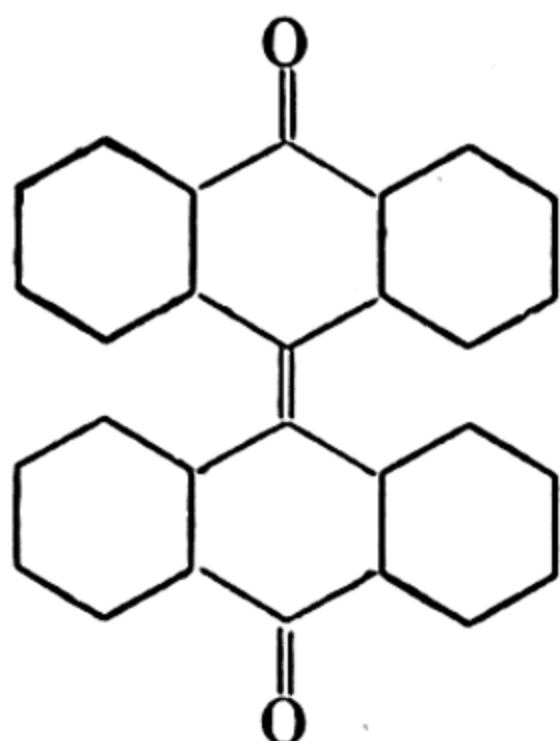


FIG. 34

raised. For example, dianthraquinone is yellow at room temperature; its solutions become green on heating and revert to the original colour on cooling. To explain this we must assume a ground state of the molecule and an excited

state, transitions between these giving the low-temperature colour, and another state between the two, reached by the acquisition of thermal energy, which gives the high-tempera-



ture colour by passing to the excited state. This intermediate molecular state has been variously interpreted as a 'radical' or as an internally ionic ('betaine') structure, the latter probably being closer to the truth, although all attempts to reduce the interpretation to a too rigid 'valency' picture are bound to be defective.

The longest-wave absorption for the series of linear ring systems benzene, naphthalene, anthracene, naphthacene, and pentacene moves towards the longer wave-lengths the larger the molecule for the reason similar to that mentioned for polyenes. Naphthacene is coloured like potassium dichromate, while pentacene resembles potassium permanganate. As the condensed ring systems grow larger, the light absorption becomes more intense and extensive, and reaches to longer wave-lengths, until in graphite we have a black substance of high opacity. The characteristic of 'conjugated' organic compounds is the existence of 'non-localized' electrons, i.e. of electrons occupying orbitals extending over more than one bond. In two dimensions in graphite, and in all three dimensions in metals, we have non-localized electrons whose orbitals stretch right through the whole crystal. A typical metal may be regarded as having its valency electrons in orbitals resembling those of the 'particle in the box' (p. 61),

the 'box' being the whole metallic crystal. There will be as many neighbouring orbitals, all very closely spaced, as there are valency electrons in the crystal, but by the Pauli principle only the lower half is filled (each orbital by two electrons). The energy differences between the millions of orbitals is so slight, though the whole band may amount to 20 k.calories in energy width, that electrons from the higher 'filled' levels easily jump to still higher 'unfilled' ones, losing their partners and becoming capable of metallic conduction and of reflecting incident light (p. 32).

In any theories of the 'colour' or absorption of light by any substance three different matters must be clearly distinguished. The first is the position in the spectrum of the absorption band, whether far in the ultra-violet, in the red, etc. This is entirely determined by the quantum relation $E = h\nu$, where E is the energy difference between two molecular orbitals. Any factor, such as increasing length of a polyene chain, which diminishes energy differences will cause the light absorption to move towards the red end of the spectrum. Replacement of CH by N or O as in the series anthracene, acridine, phenazine, xanthoxonium and phenazoxonium ions, or in the dyes uranin, acriflavine, safranin, rhodamin, and resorufin, causes little change in the absorption band position; the N and O compounds absorbing at slightly longer wave-lengths (Fig. 35). This effect is rather more marked in the azobenzene, benzalaniline, stilbene group, all of which absorb strongly at 3,100 Å, but in the first two the absorption is prolonged to longer wave-lengths. The orbitals of these analogous compounds are therefore essentially similar, but a small amount of 'coupling' or 'merging' of the 'lone pair' or non-bonding electrons of the N or O with the π electrons of the ring diminishes the orbital energy differences somewhat. If a substance has *two* 'light absorbing centres', such as a benzene ring and a carbonyl group, its absorption resembles the simple sum of the separate absorptions (e.g. a

band at 2,500 Å for the benzene ring and one at 3,000 Å for the carbonyl group) if the groups are unconnected by 'conjugation'. If the groups are conjugated the separate 'orbitals' lose their identity in a new system, and the light absorption consists of an entirely different band of much longer wavelength. A large conjugated system such as a porphyrin has an absorption band system very little affected by substituents,

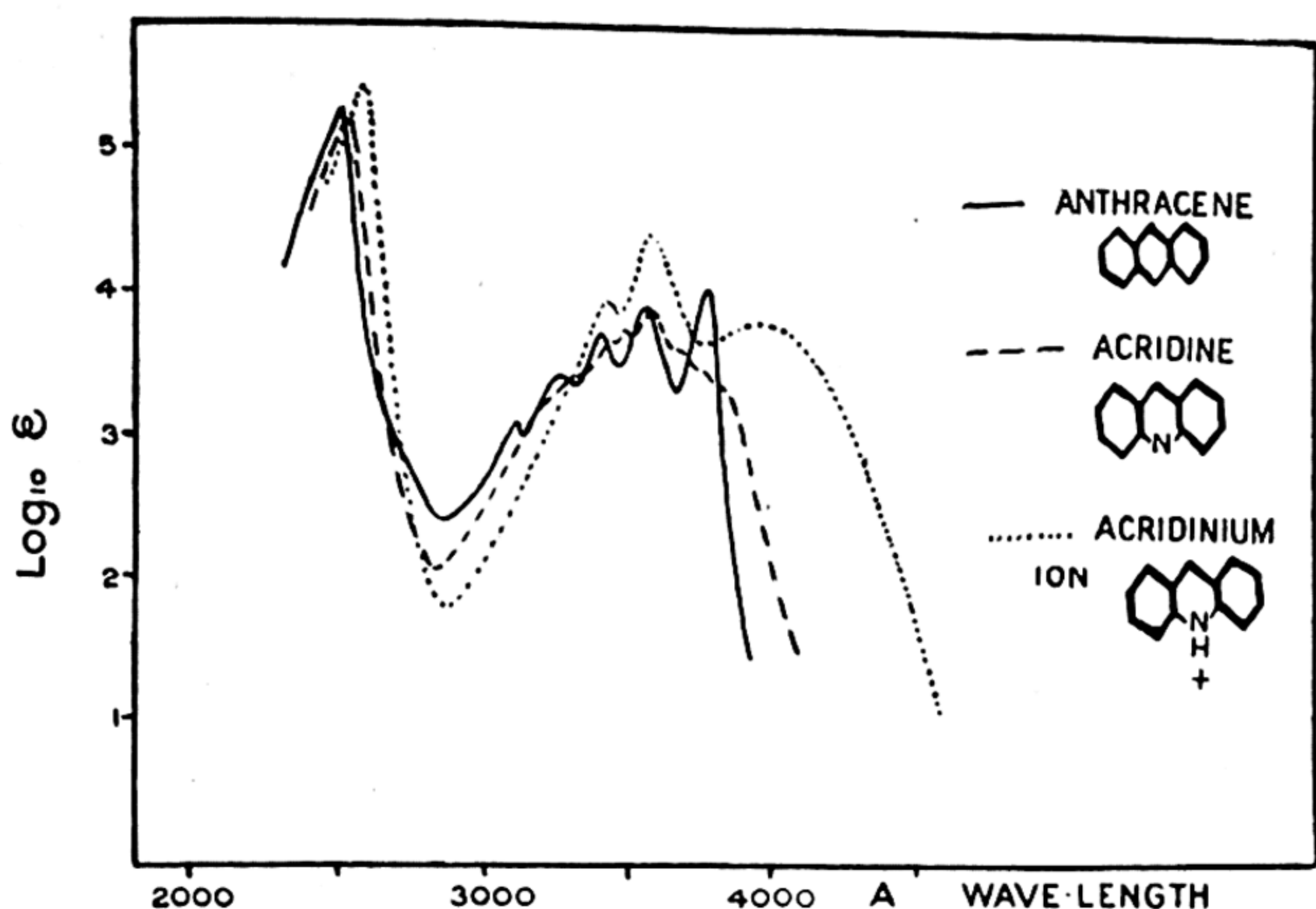


FIG. 35. Absorption spectra of anthracene and acridine solutions.

unless these join in the conjugation. Under favourable conditions therefore the presence of certain conjugated molecular groupings are recognizable spectroscopically even if the actual substance has different substituents from that chosen as the 'type'. In different types of compound, conjugation can vary in degree, i.e. the 'non-localization' of electrons can be more or less complete. The degree of conjugation is determined by the similarity or dissimilarity of the conjugating parts judged from an energy-level standpoint.

The second matter relating to absorption bands is the *width* and *shape*. Certain absorption bands are narrow and

others are wide; some fall off more steeply on the 'red' side than the 'blue'. This is determined by the shape and disposition of the vibration-energy curve of the upper level. Fig. 19 illustrates the matter for a diatomic molecule. The poly-dimensional energy surfaces of more complex molecules are not known quantitatively, but the same principles apply. By the Franck-Condon principle, absorption at ordinary temperature corresponds to the energy jump along the vertical centre line. If the upper level has almost identical internuclear distances with the lower level (as with highly conjugated systems such as dyes, porphyrins, etc.), the upper level is reached at its flat minimum, and a narrow band results. If the upper curve is met on its left-hand side, however, as in Fig. 19, the band is wider through the simultaneous excitation of upper level vibrational frequencies, and is steeper on the longer-wave side. The maximum absorption lies as shown on the right of the diagram, and the lateral extent depends upon the degree to which the maxima of the curves representing the vibrations of the upper state overlie the vertical Franck-Condon line. In such qualitative terms one can picture how it is that dye bands are widened by certain substituents (e.g. Br) and narrowed by others (e.g. F), and the shape of the band altered in various ways.

The third matter is the *intensity* of the absorption. This is measured as the total area under the absorption band (including all its vibrational structure) when the extinction coefficient is directly plotted against frequency. Theory shows that the quantity $\int \epsilon d\omega$ cannot exceed $2.3 \times 10^8 \text{ cm.}^{-1}$ for a transition of one electron. Since the integral approximately equals $\epsilon_{\text{max}} \Delta\omega$, where ϵ = molar extinction coefficient and $\Delta\omega$ = half-width of band, and half-widths of absorption bands are usually about $2,000 \text{ cm.}^{-1}$ in magnitude, the maximum value of ϵ is about 10^5 . This value is reached for many conjugated organic substances, but bands often occur with much smaller areas and values of ϵ_{max} . Such cases of

relatively weak absorption are characterized by 'oscillator strengths' f of less than unity, or, expressed alternatively, low 'dipole strengths of transition' D . $f = 1.08 \times 10^{11} D \omega$. The dipole transition strength D is closely related to the square of the dipole moment of oscillation of the vibrator concerned. For example, if a $1s$ hydrogen atom absorbs light to give a $2p$ atom, the alternate side to side oscillation of the $2p$ wave endows the atom with a dipole moment which it did not have in the $1s$ level. Unless a dipole moment of such a kind is generated or destroyed, electromagnetic radiation cannot be absorbed or emitted (see Figs. 17 and 30). For this reason certain transitions are 'forbidden', e.g., $1s \longleftrightarrow 2s$. It should be noted that the dipole concerned is not a permanent one in the usual sense. The opposite ends of the atom or molecule have not fixed charges but correspond to rapidly alternating electric waves. The dipole moments are in principle calculable from the wave-mechanical equation, though in fact they can be estimated only in simplified examples. A general point of importance is the effect of *symmetry*. The 2,600 Å absorption band of benzene (p. 116) is forbidden for a perfectly hexagonal molecule, owing to the lack of a transition moment. In solid benzene at liquid hydrogen temperatures it may be observed as a very weak band through the slight distortion of the molecules from perfect symmetry by crystal forces. In liquid or dissolved benzene at the ordinary temperature it is a band of moderate strength owing to the superimposed effects of certain vibrations of the atomic skeleton. Substituted benzenes have a stronger absorption than benzene itself, owing to the further disturbance of symmetry. Three stages in the alteration of the absorption of benzene by substituents may be distinguished: first, 'inert' substituents like $-\text{Cl}$, which increase the band strength without much altering the wave-length range; second, substituents which 'conjugate' with the ring, as $-\text{NO}_2$ or $-\text{CHO}$, and produce a new system of orbitals with

much longer-wave and more intense absorption, and third, substituents like $-I$, $-OH$, or $-NH_2$, which behave in an intermediate manner through the *partial* coupling of the electron clouds of their 'lone pairs' with the π electron clouds of the ring (see Fig. 36) (cf. p. 121). *Cis* and *trans* forms, as of stilbene or azobenzene, have different absorption intensities because of their different transition moments.

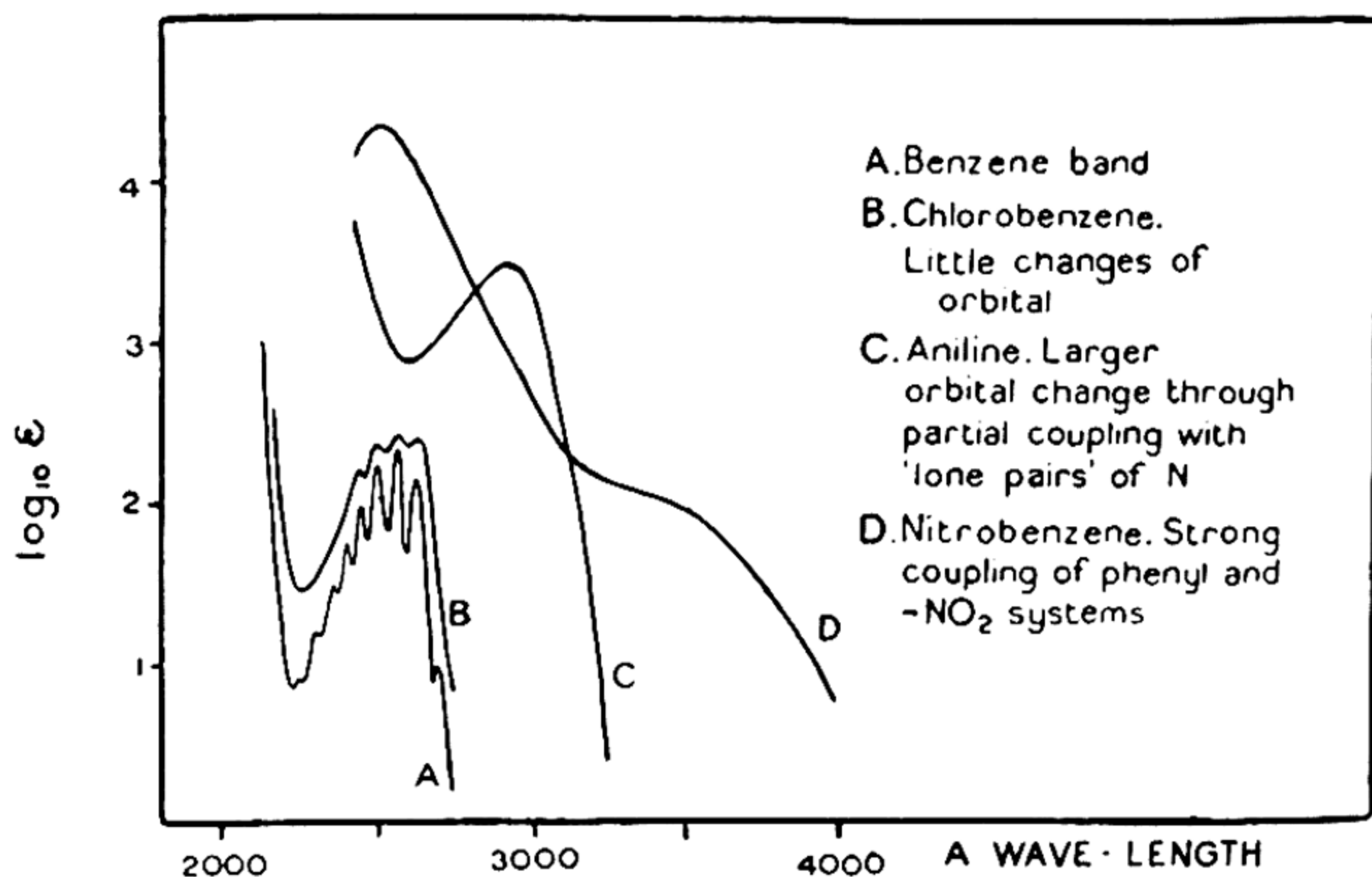


FIG. 36. Absorption spectra of solutions of substituted benzenes.

For the longest-wave band the *trans* is more intense, since the moment is directed along the zigzag molecule, and the *cis* is a shorter form. In shorter-wave bands, where the moment is differently directed, the *cis* may absorb the stronger.

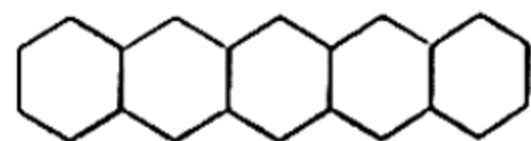
The determination of transition strengths for gases from the integral $\int \epsilon d\omega$ is sometimes rendered difficult because the absorption band consists of exceedingly narrow rotation lines of very high extinction coefficients, and the contours of these lines are not revealed by ordinary spectrographs. The effect may be shown by exhausting with a filter-pump a flask containing a few crystals of iodine. The vapour appears colourless in white light because of the

excessive narrowness of the absorption lines. If air is now admitted, the molecules are 'detuned' by collisions and the absorption lines broadened, so that the vapour appears pink. Though more of the white light is being absorbed when air is present, the above integral is little affected, and it should not be concluded that the air renders iodine a more *intense* absorber.

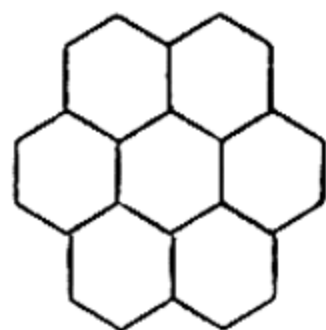
The absorption spectra of aldehydes and ketones are interesting because of the photochemical reactivity of these substances. The formaldehyde molecule resembles ethylene, the C=O link replacing the C=C. Absorption occurs at about 1,900 Å, and this is identified with a transition analogous to the ethylene absorption at 1,750 Å, i.e. one electron from the π orbital is excited to the antibonding orbital, $\pi_u \rightarrow \pi_g$, developing a new node perpendicular to the molecular plane. These substances also show a weak but characteristic absorption near 3,000 Å which is not paralleled by ethylene. The transition involved seems to be the excitation not of a π valency electron but of one of the electrons in the 'lone pairs' on the oxygen, which are non-bonding electrons in approximately atomic p levels, to the unoccupied π_g molecular orbital. In diazomethane, CH_2N_2 , which has a yellow colour, we have an example of a substance absorbing at long wave-lengths where the effect cannot be ascribed to the production of small energy differences between orbitals as with highly conjugated polyenes. The transition involved in the colour is possibly, as with aldehydes, the passage of an electron from a non-bonding orbital on a nitrogen atom to a π_g molecular orbital between the nitrogens. The bands associated with this type of transition usually have extinction coefficients considerably lower than those of the polyene or other conjugated molecule transitions. The long-wave, low-intensity diazomethane band may be a singlet-triplet transition; triplet levels lie lower than corresponding singlets.

The possession by a molecule of a relatively 'free' electron

usually leads to deep colour, of long wave-length because orbital energy differences are small and of high intensity because the 'transition moment' is high in the electron shift. This effect reaches its limit in metals, the high absorption appearing as metallic reflectivity, since the light absorbed is not degraded to heat (p. 33). Radicals are usually highly coloured, and nitric oxide is the only molecule with an odd number of electrons which is not coloured in the visible region. We may contrast the coloured 'odd' molecules NO_2 and ClO_2 , and the sodium atom, with the colourless ions NO_2^- , ClO_2^- , and Na^+ . Oxygen, whose molecule may almost be considered a diradical since two electrons have uncoupled spins in the ground state, absorbs at much longer wave-lengths than nitrogen. Nitroso-compounds, as nitroso-benzene or the compound $\text{K}_2(\text{SO}_3)_2 \cdot \text{NO}$, are deeply coloured when in the monomeric liquid or dissolved state; on crystallization such compounds often lose their colour through forming dimeric molecules with no 'odd' electron. The latter substance, for example, gives purple solutions and pale yellow crystals. If we compare the absorptions of anthracene with phenanthrene (Fig. 37), or of pentacene



(1st max. at $5,755 \text{ \AA}$) with coronene (strong ab-



sorption beginning about $4,000 \text{ \AA}$), we note that in each case the first substance has a much longer-wave absorption which must be related to the fact that the second substances of the pairs have 'aromatic' structures while the former can be written as 'diradical' structures. The energy levels of molecules with non-spin-paired electrons are closer together than those of similar more normal molecules. Liquid sulphur just above the melting-point is pale yellow, the molecules here consisting of saturated S_8 rings. On heating, the rings open up to give radicals which give rise to the darkening of colour

and to the polymerization which causes the increase in viscosity peculiar to this liquid. The triphenylmethyl radical absorbs at much longer wave-lengths than triphenylmethane, being yellow in colour. In some solvents it can be obtained in the ionized form. The cation, having lost an electron, has a light absorption almost pushed back into the ultra-violet, while the anion, with an additional electron, is dark red in colour.

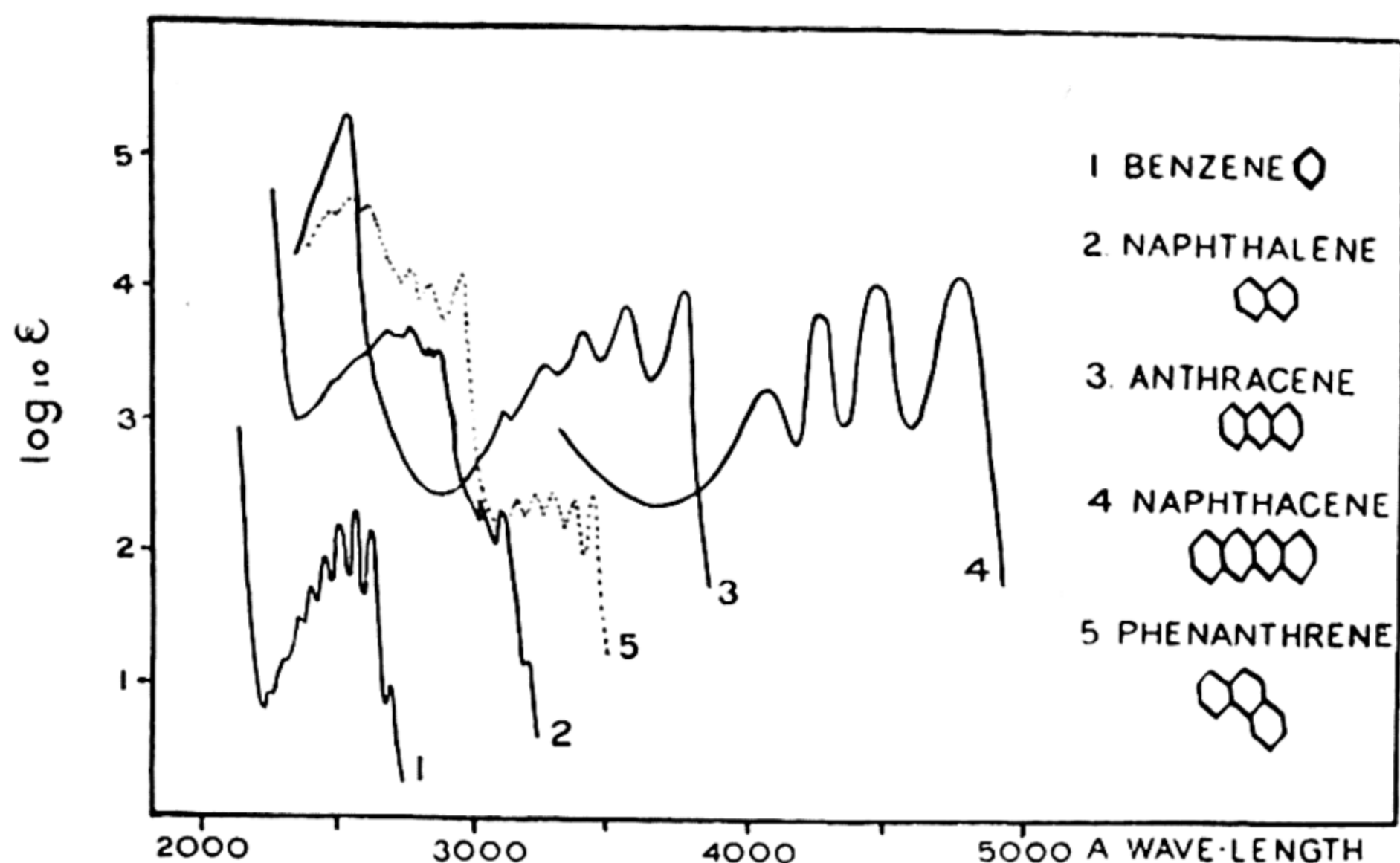
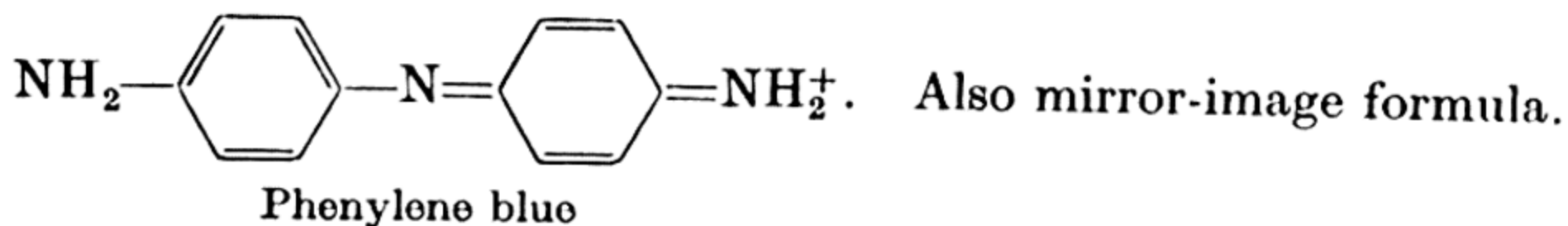


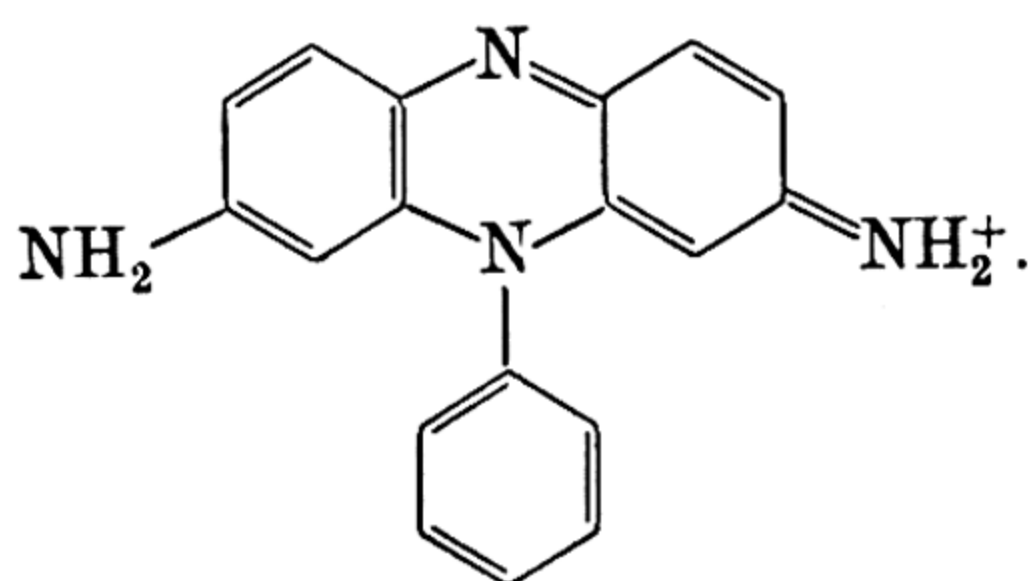
FIG. 37. Absorption spectra of solutions of aromatic hydrocarbons.

The organic compounds used as dyes excite the greatest interest in theories of light absorption. Very many classes of dyes are known, of widely different formulae, but they all possess two features in common, (a) they have two or more 'polar' groups, and (b) they can be described by two or more alternative 'valency structures'. These points are illustrated by the following representative examples.

1. Quinone-imine dyes (ions).



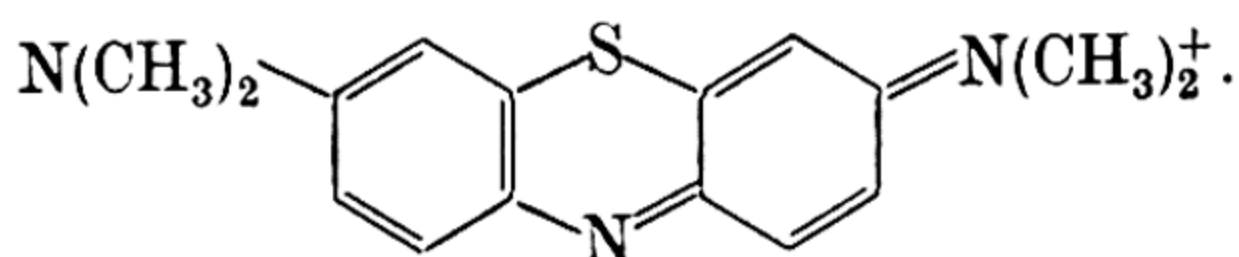
2. Azine dyes (ions).



Safranin

Also mirror-image formula.

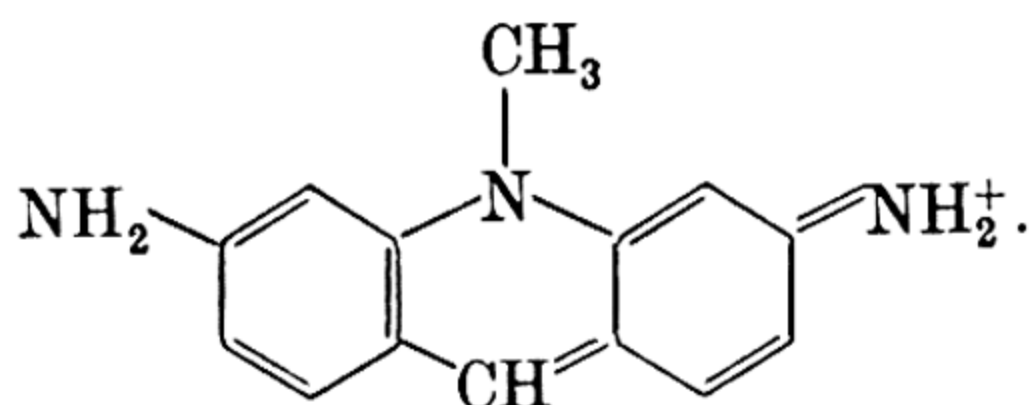
3. Thiazine dyes (ions).



Methylene blue

Also mirror-image formula.

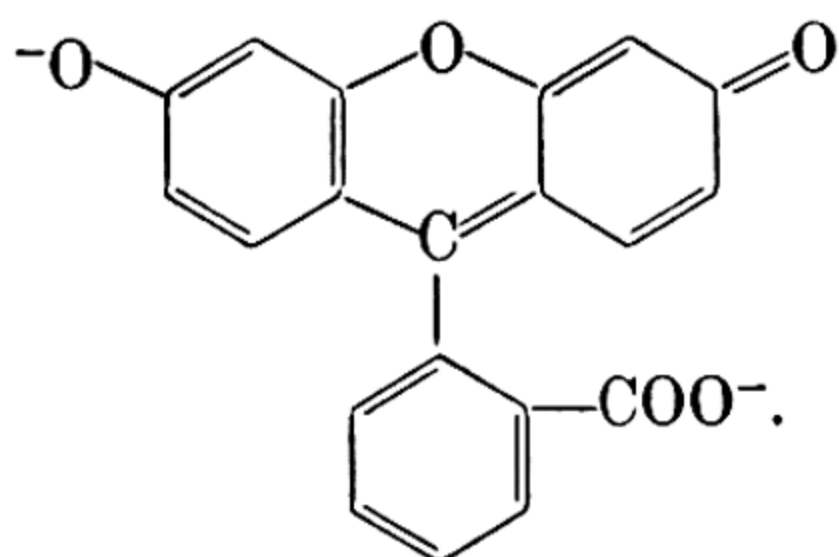
4. Acridine dyes (ions).



Acriflavine

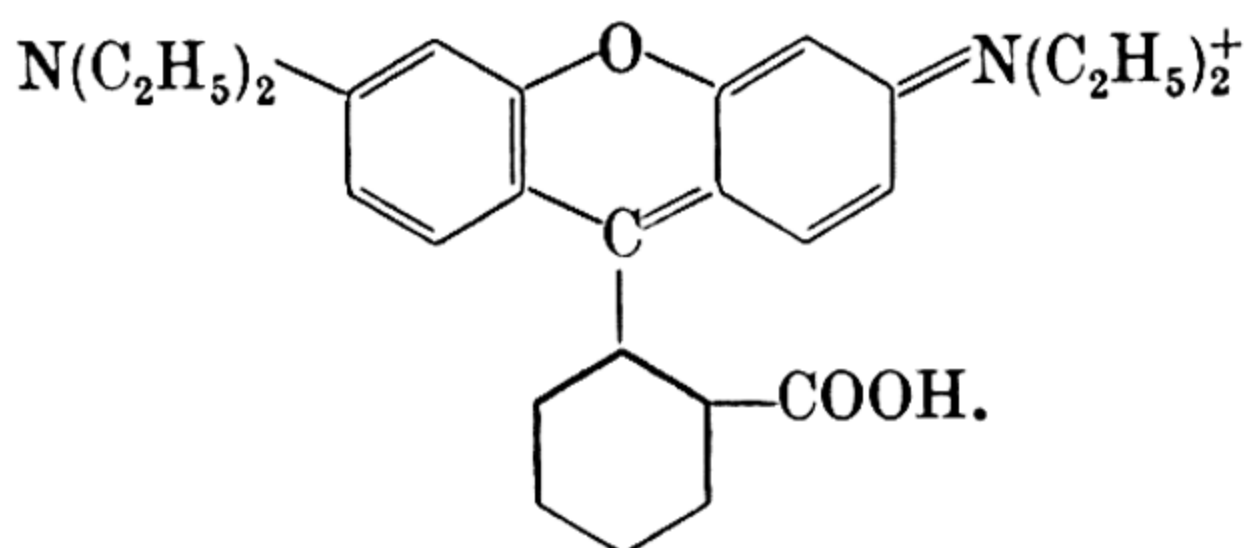
Also mirror-image formula.

5. Xanthene dyes (ions).



Uranine

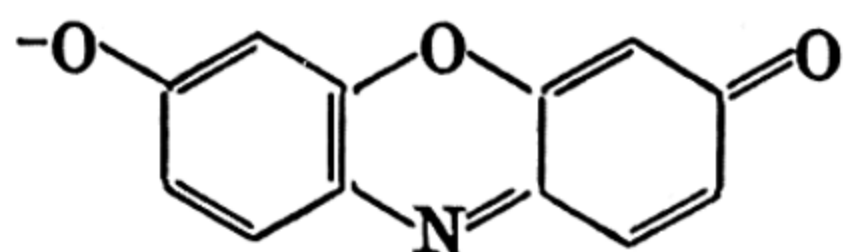
Also mirror-image formula.



Rhodamine B (3 B = ethyl ester)

Also mirror-image formula.

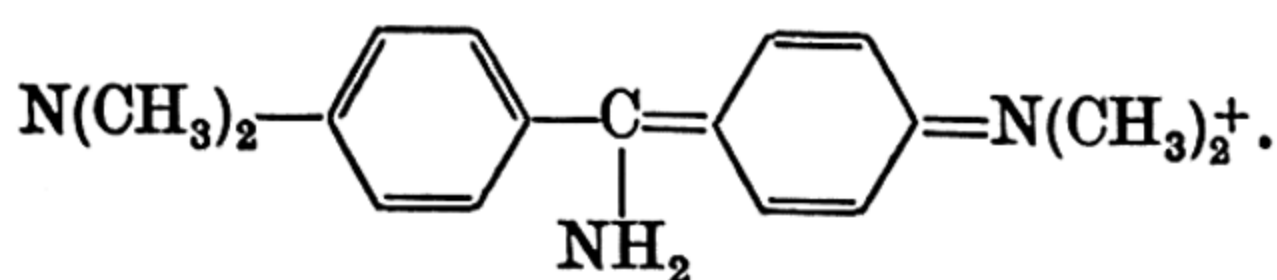
6. Resorufin dyes (ions).



Resorufin

Also mirror-image formula.

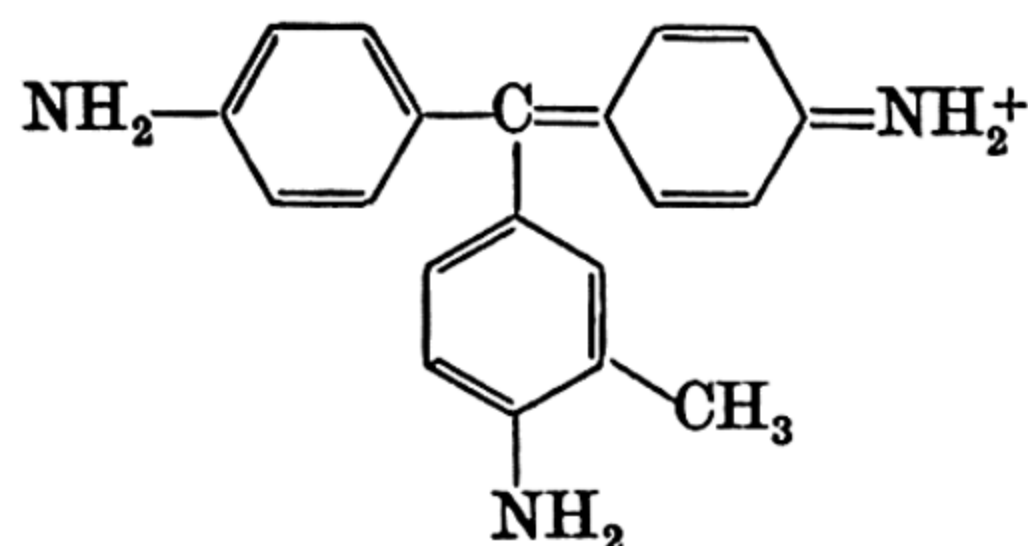
7. Auramine dyes (ions).



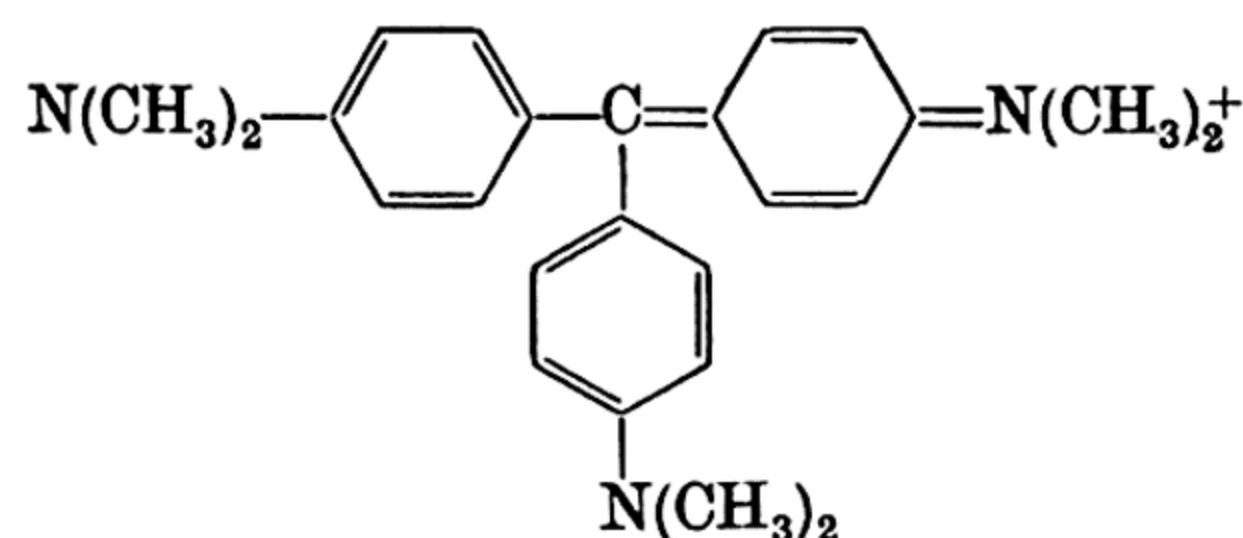
Auramine

Also mirror-image formula and one with + charge on NH_2 , another with charge on central carbon atom.

8. Triphenyl methane dyes (ions).



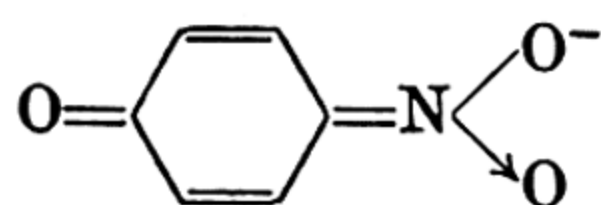
Magenta



Crystal Violet

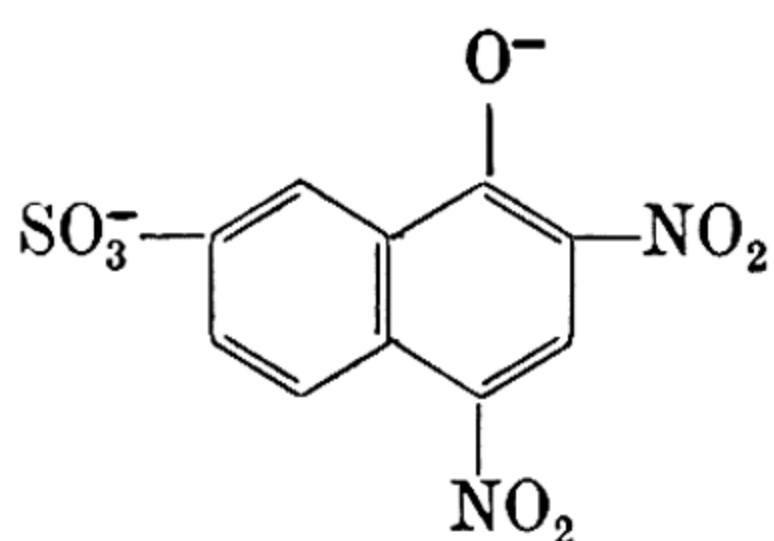
Also formulae with + charge on different nitrogen atoms or on carbon.

9. Nitro-dyes (ions).



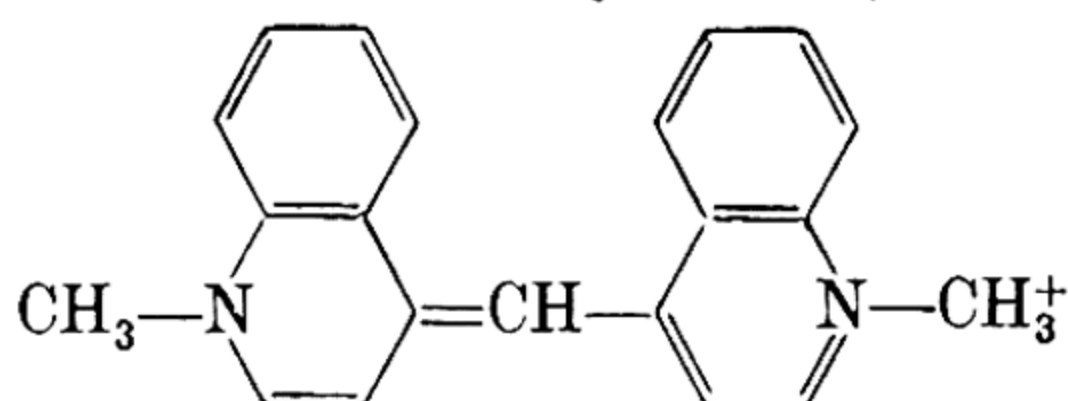
p-nitrophenol

Also non-quinonoid formula with — charge on phenolic oxygen.



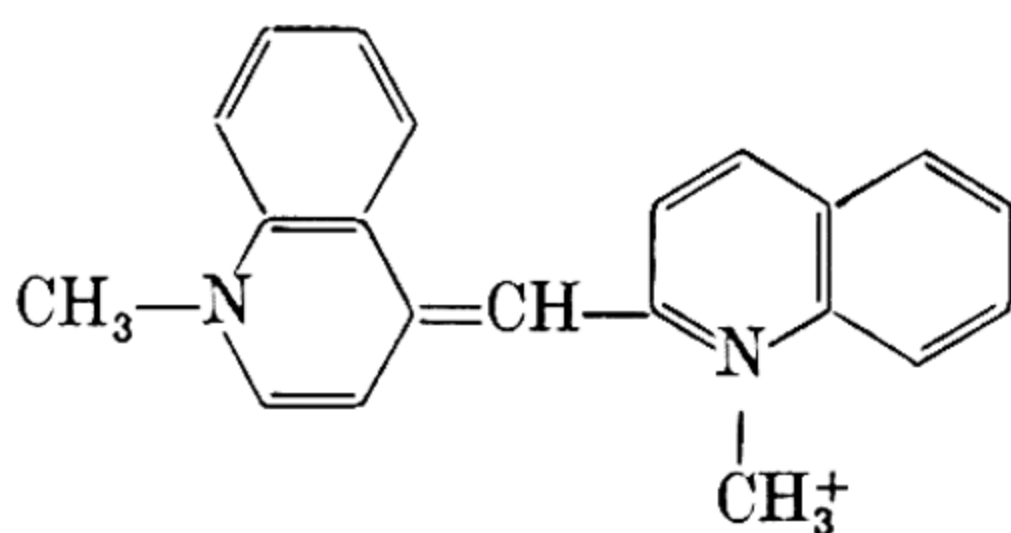
Naphthol yellow S

10. Quinoline dyes (ions).

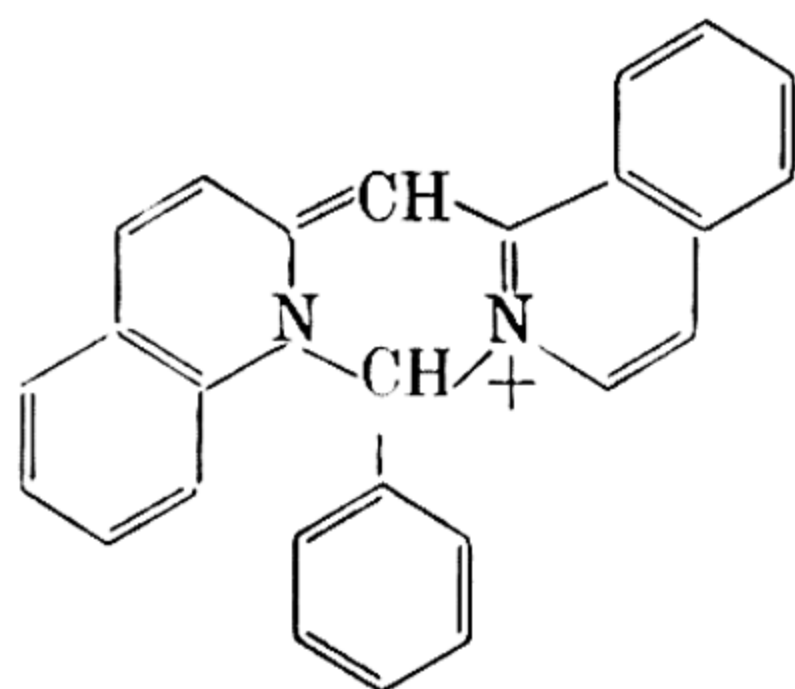


Quinaldine cyanine or Ethyl red

Also mirror image formula.



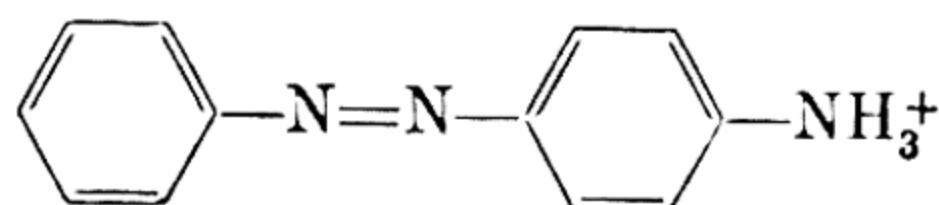
Isocyanine



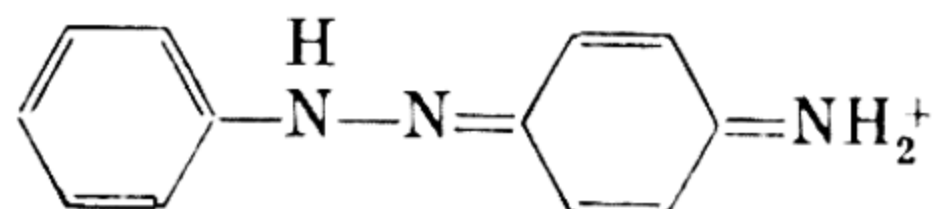
Quinoline red

Also formulae with + charge on other N or CH groups.

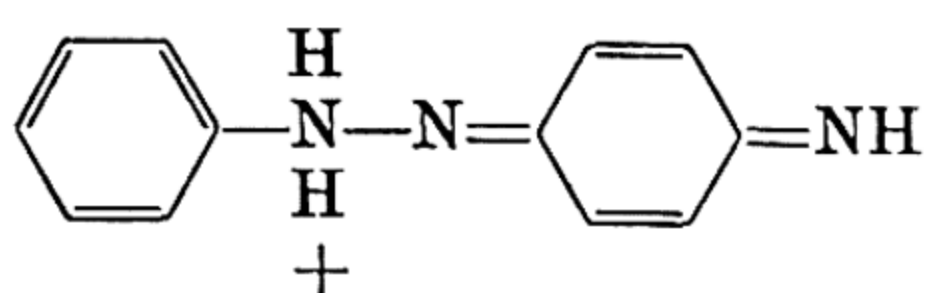
11. Azo dyes (ions).



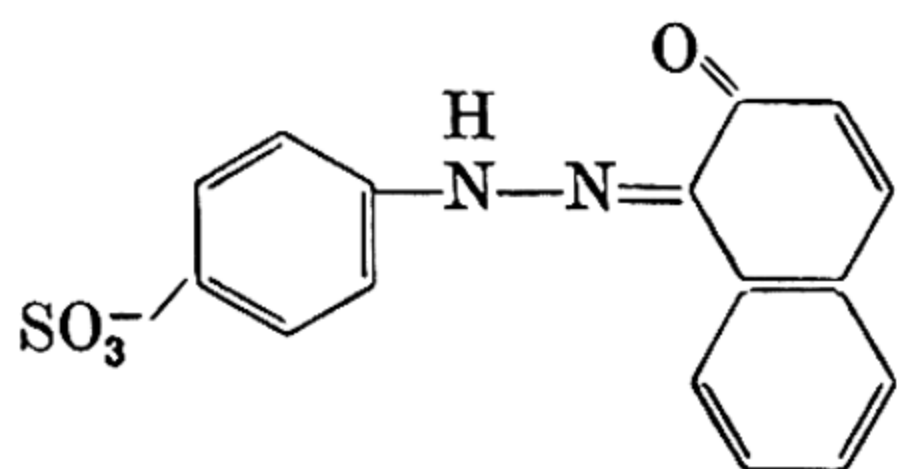
or



or

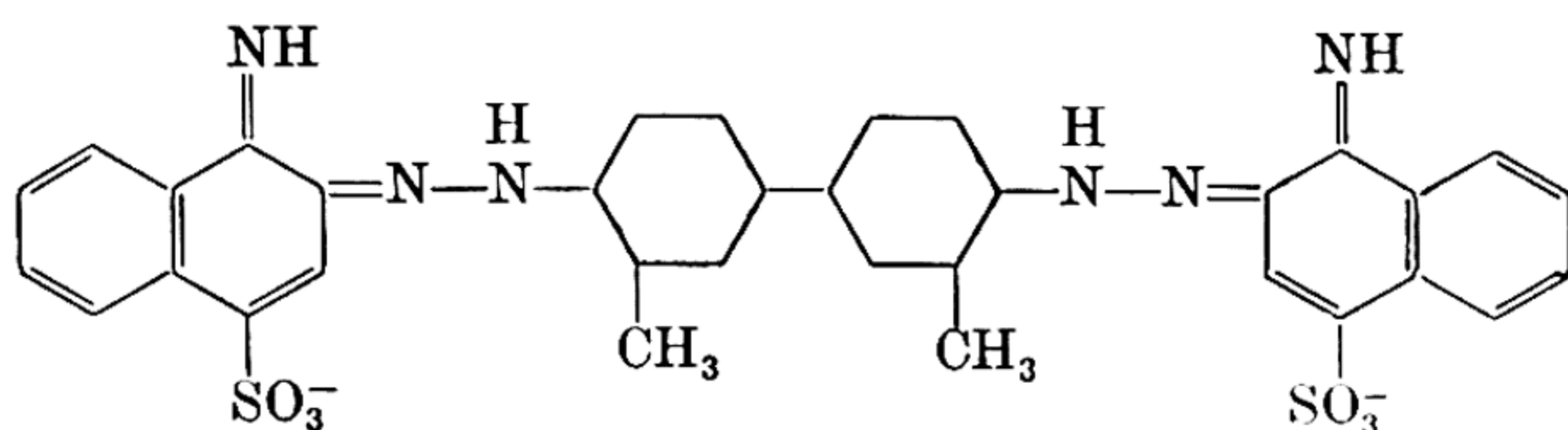


Amino azo benzene or Aniline yellow.



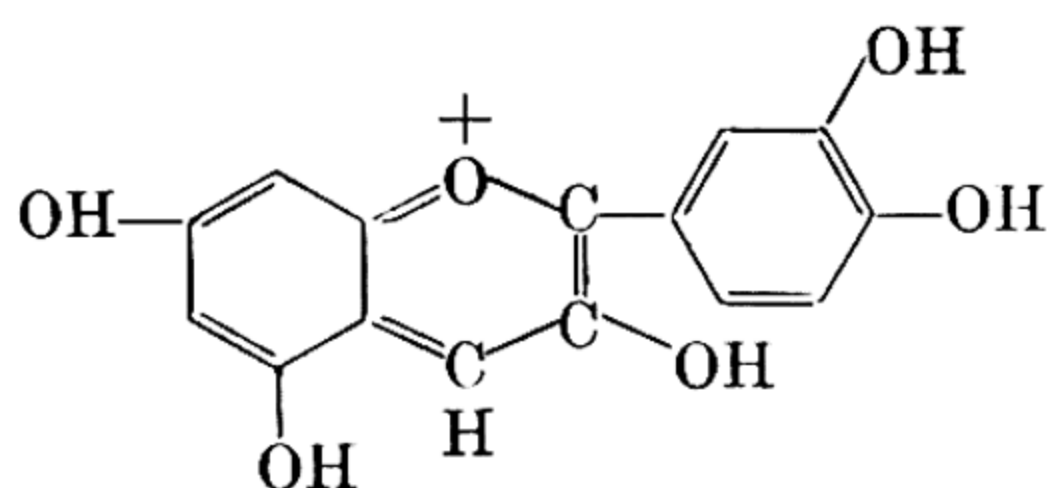
Also variants as above.

Orange II



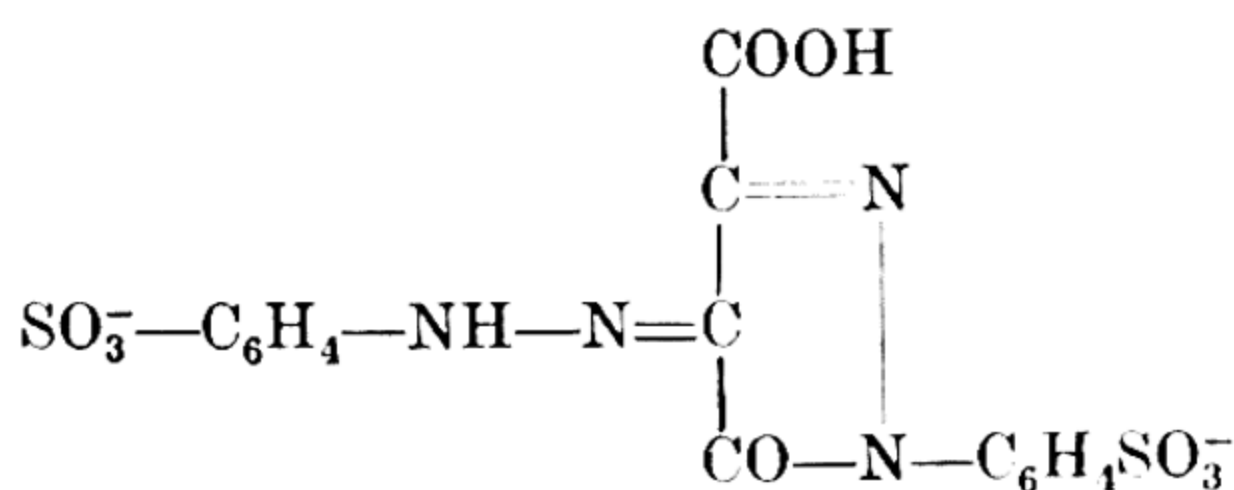
Benzopurpurin 4 B

12. Flavones (ions).



Also formulae with + charge on C atoms.

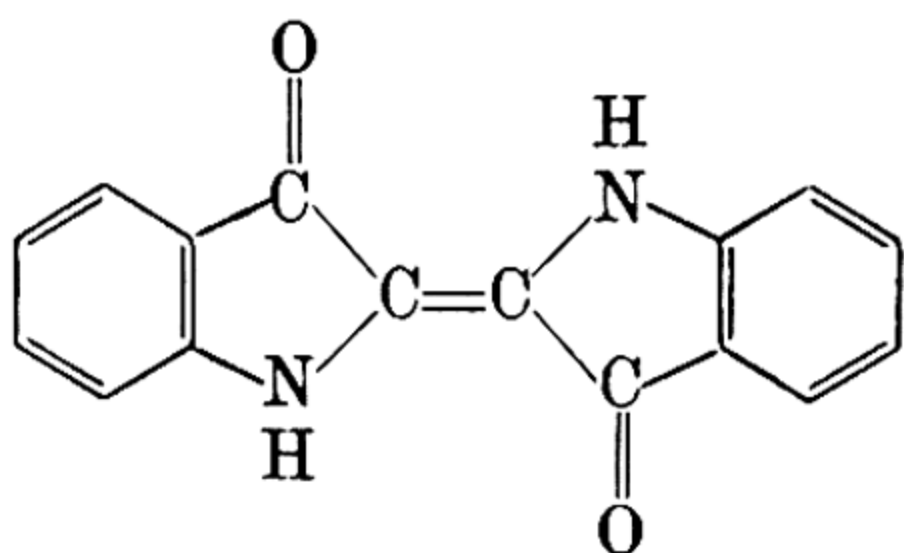
13. Pyrazolone dyes (ions).



Also azo formula.

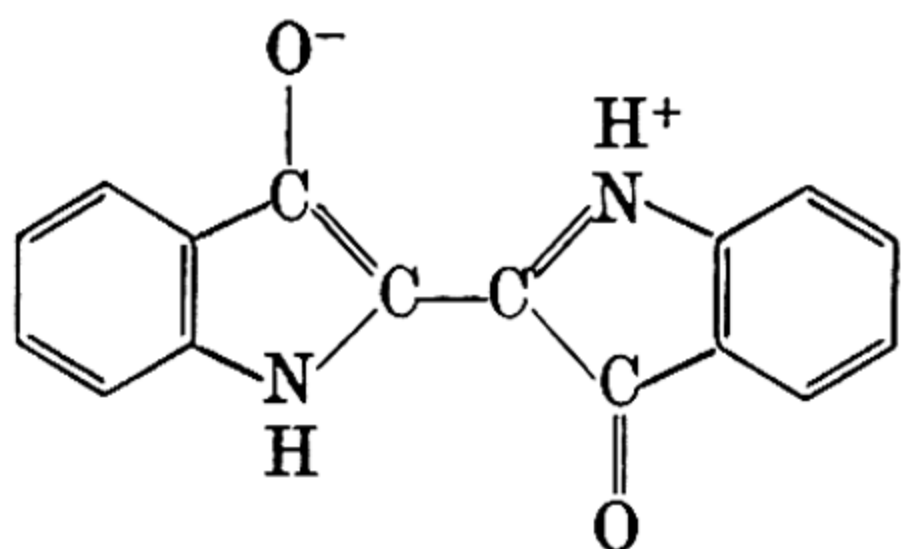
Tartrazine

14. Indigo dyes (inner molecular ionoid).



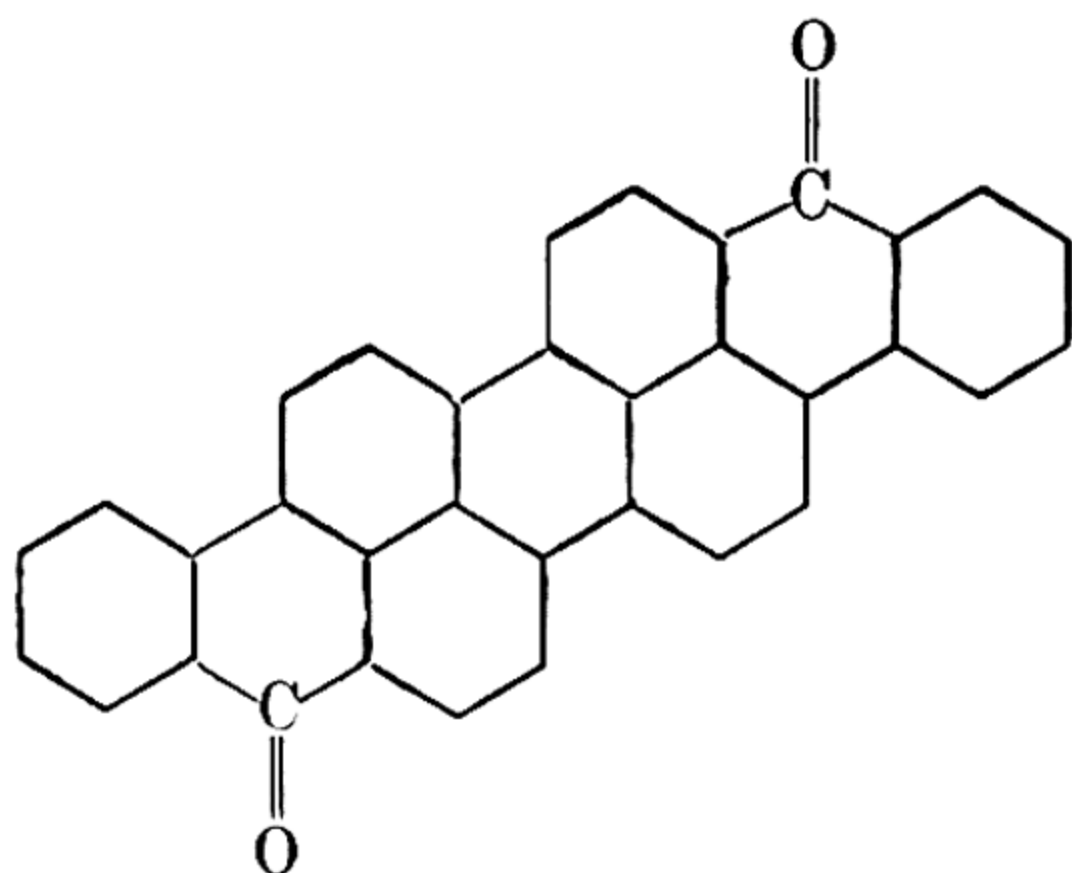
or

Also other ionoid forms.



Indigo

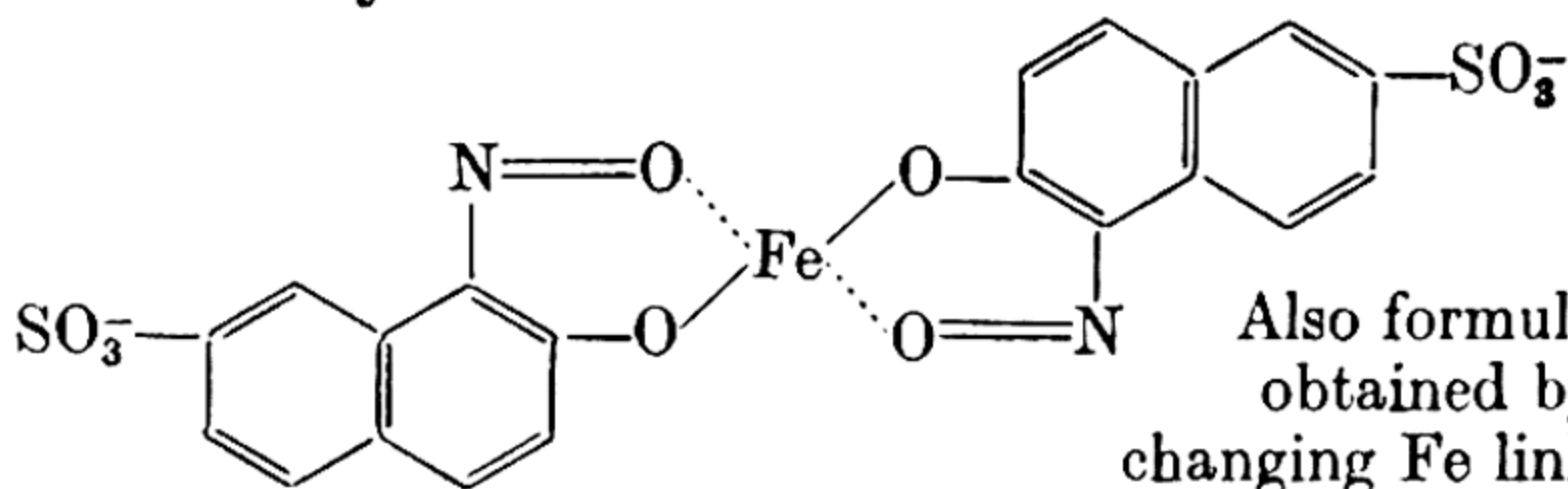
15. Benzanthrone dyes.



Caledon Brilliant Purple R

Also ionoid forms.

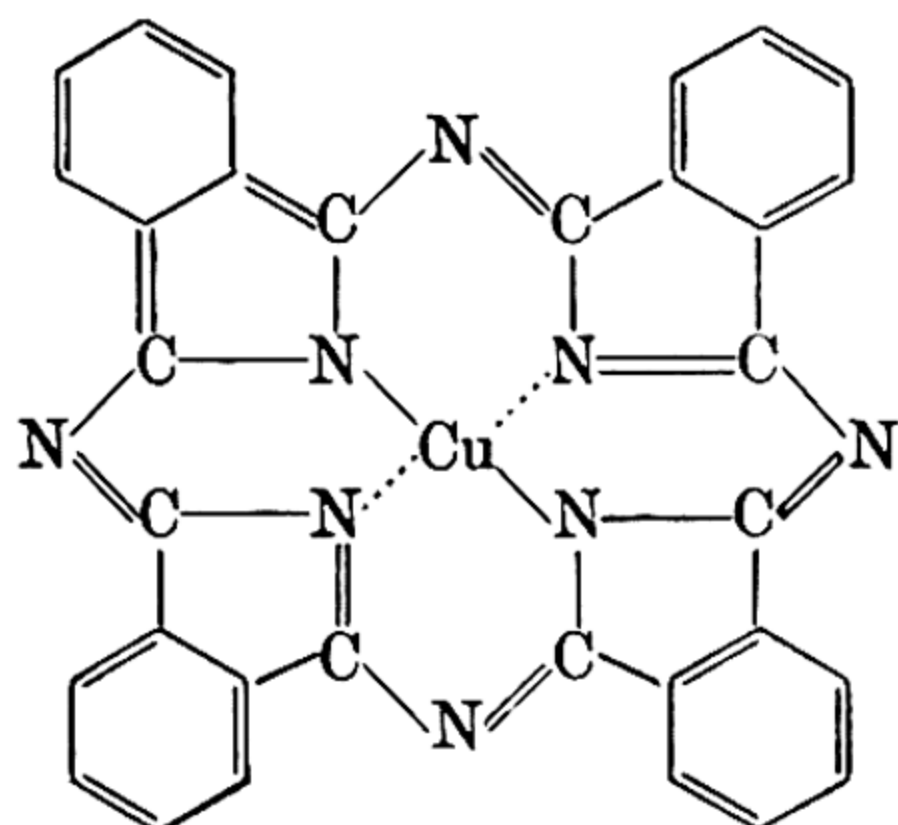
16. Nitroso dyes.



Naphthol green B (Iron lake)

Also formulae
obtained by
changing Fe linkages.

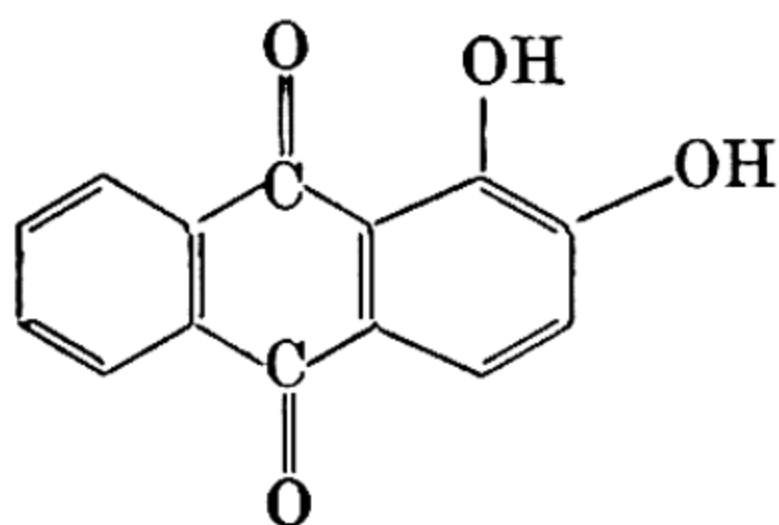
17. Phthalocyanines.



Monastral Fast Blue B

Also formulae obtained by
changing Cu linkages.

18. Anthraquinone dyes.



Alizarin

Dye used as a metallic lake with
variants as above.

Owing to the intractability of rigorous wave-mechanics the relations of colour to structure must be treated by approximate methods. New concepts are necessarily introduced, and although the conclusions of different treatments must mean ultimately the same thing, it is sometimes not easy to translate one set of views into another. The physicist naturally turns to a *molecular orbital* method. The molecule of hydrogen in its ground state is imagined to have the two electrons in a σ_g orbital; an excited level has one electron in a higher orbital, as σ_u (p. 111). Conjugated organic molecules are regarded as possessing non-localized π electrons whose orbitals may be simplified to resemble linear vibrations with polyenes and vibrations in a flat cylindrical box with benzene, for that in effect is what the methods of p. 115 amount to. The π orbitals are 'occupied' by electron pairs, and absorption

of long-wave light causes an electron to pass from the highest filled orbital to the next unfilled one (Fig. 32). Since the successive orbitals grow closer in energy differences, molecules with large numbers of π electrons, as dyes, would be expected to absorb long-wave, i.e. visible, light. The polar groups of dyes produce the asymmetry necessary to render the transitions 'permitted', and the transition moment is high because the light absorption sends an electron to a higher orbital with a new node across the molecule, and the size of the molecule and the polar groups ensure that the excited electron 'vibrates' across a considerable distance. For example, the *p*-nitrophenol molecule has a strong band in the near ultra-violet because of its π electrons. Its ion absorbs at longer wave-lengths because by the loss of H^+ the oxygen atom is rendered negative so that its 'lone pair' of *p* electrons with nodal plane coinciding with that of the ring are driven over to associate with the π electrons of the ring, becoming 'delocalized'. The intensity of the absorption, and therefore the transition moment, is only slightly increased (Fig. 38, left). Azobenzene shows two bands in its absorption spectrum, a relatively weak one at 4,480 Å and a stronger one at 3,130 Å. The first is probably due to a transition of a non-bonding N electron to an antibonding $N=N$ orbital and the second to a transition $\pi_u \rightarrow \pi_g$ of the $N=N$ orbital (cf. p. 125). In *p*-aminoazobenzene the first band is much more intense but unchanged in wave-length, while the second is not so markedly increased in strength, but is moved to much longer wave-lengths (3,620 Å). The substituent increases the transition moment of the first band by some effect of its polarity, while its chief influence on the second band is one of increasing the conjugation, by increased coupling between the *p* and π electrons of the amino- and the azo-groups, so lengthening the orbital of the excited electron, and diminishing the energy of the transition. The wave-length of the first band is, however, affected by ionization. The curves on the right

of Fig. 38 illustrate the long-wave absorption of the related substance methyl orange (*p*-dimethyl amino-azobenzene *p'*-sulphonic acid), a typical hydrogen ion indicator. The long-wave azo-band is moved to longer wave-lengths in the cation compared to the molecule; basic ionization here

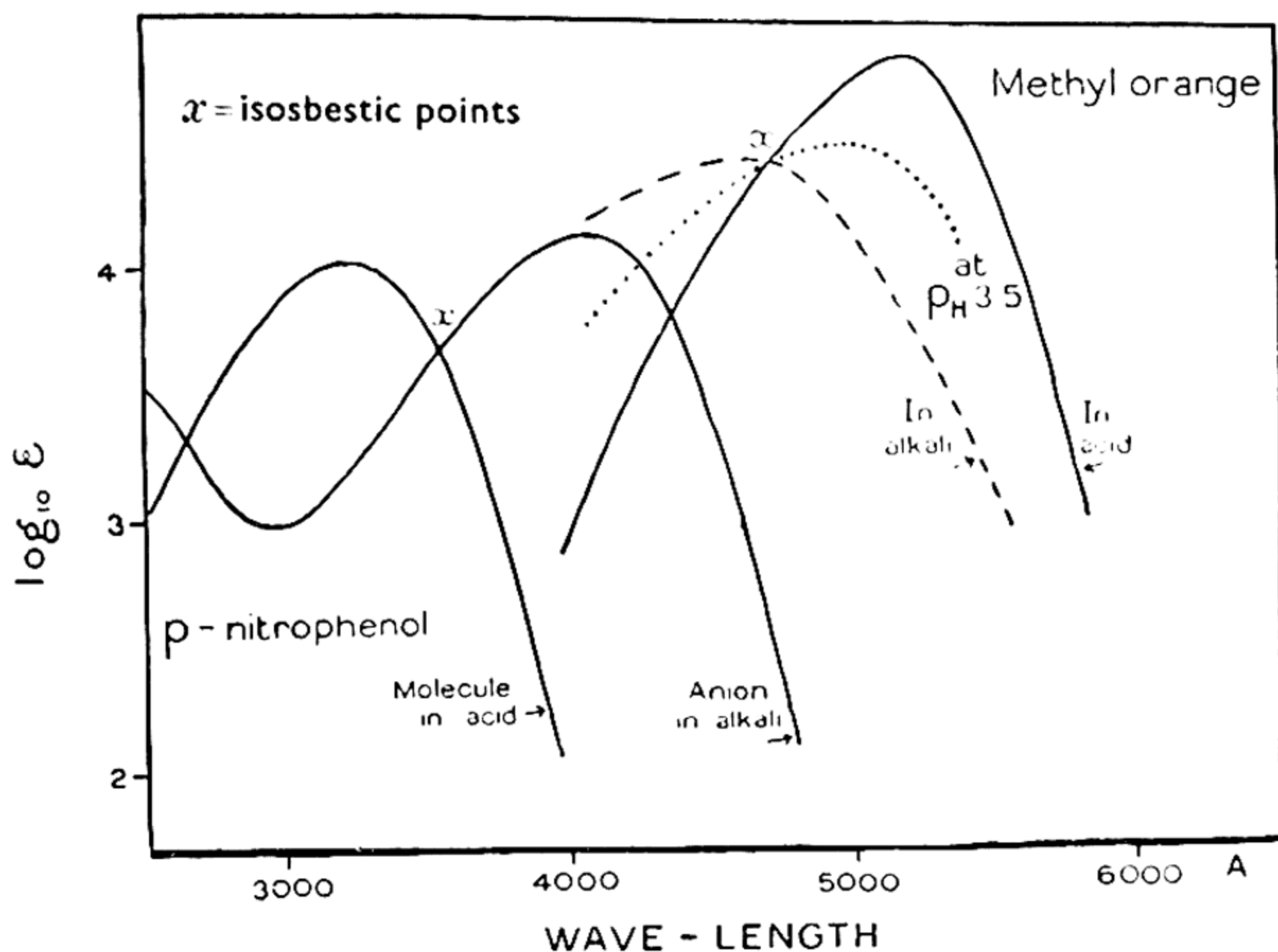


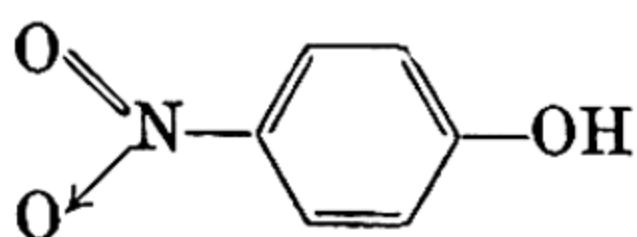
FIG. 38. Absorption spectra of indicators at different pH values

permits of a greater degree of conjugation which lowers the energy of the electronic transition on light absorption, as in the case of *p*-nitrophenol anions.

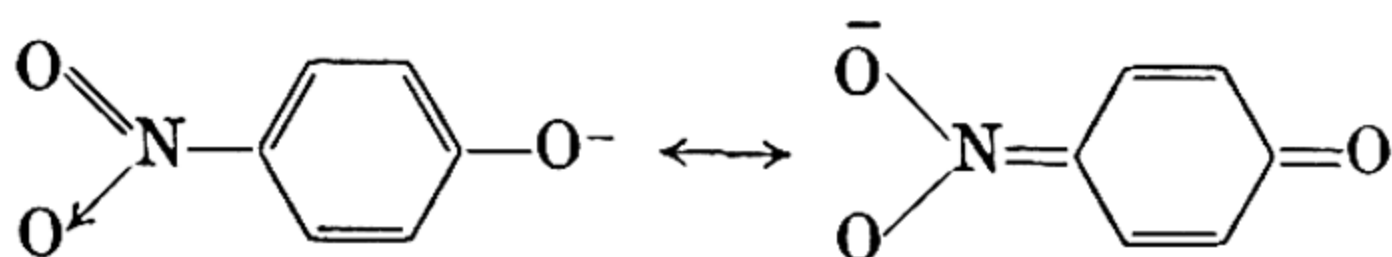
The chemist has long been accustomed to represent molecules by *valency formulae*, and therefore may prefer to the molecular orbital treatment a method of approximation which does not entirely abandon the concept of valency links. On this view the normal hydrogen molecule consists of two atoms with overlapping atomic orbitals forming a link, while an excited level may be regarded as H^+H^- , the charge passing to and fro (cf. p. 123). In this alternative treatment the concepts employed are quite different, and

it may appear difficult to relate them to their equivalents of the molecular orbital approximation. Conjugated organic molecules on the alternative view are conceived of as having an internal 'oscillation' to and fro. The true structure of butadiene, for example, is approximated to by writing down all reasonable *valency* structures, i.e., the 'ordinary' formula and various 'ionoid' forms with separated electronic charges $+$ and $-$ located on the carbon atoms. The molecule is then regarded as a 'resonance hybrid' of all the forms. Benzene is imagined as a resonance hybrid of the two Kekulé structures, the three Dewar structures, and ionoid structures. The question of the 'reality' of the 'resonance between valency structures' is meaningless since the whole treatment is only an approximation. An excited molecular level produced by light absorption appears on this method as another resonance hybrid of the valency structures with different 'proportions' of the components. For example, the ground level of the benzene molecule may be said to be 'composed' of about 39 per cent. of each of the two Kekulé structures, 7 per cent. of each of the Dewar structures, and a small amount of ionoid structures; in an excited level the proportions of the Dewar and ionoid structures are much greater. These 'proportions', of course, are nothing more than hypothetical aids in the mathematical treatment. The problem is reduced and simplified mathematically to the combination of the valency formulae into a single composite, as a set of coupled vibrators may be combined to give the properties of a single resultant vibrator. The energy of the lowest molecular level is found to be lower than that calculated for any of the valency structures, i.e. *resonance* may be said to increase *stability*. The greater the *resonance*, i.e. the more imaginary structures of nearly equal energy which may be assumed to participate in the real structure, the more upper levels there are, and the closer do they lie together. Consequently 'strong resonance' gives long-wave light absorp-

tion, and an analogue of the transition moment explaining intensity of absorption can be found in the charge shift in the different valency structures. The longer-wave absorption of the ion of *p*-nitrophenol compared with the molecule here appears as due to the increased resonance possibilities of the ion:



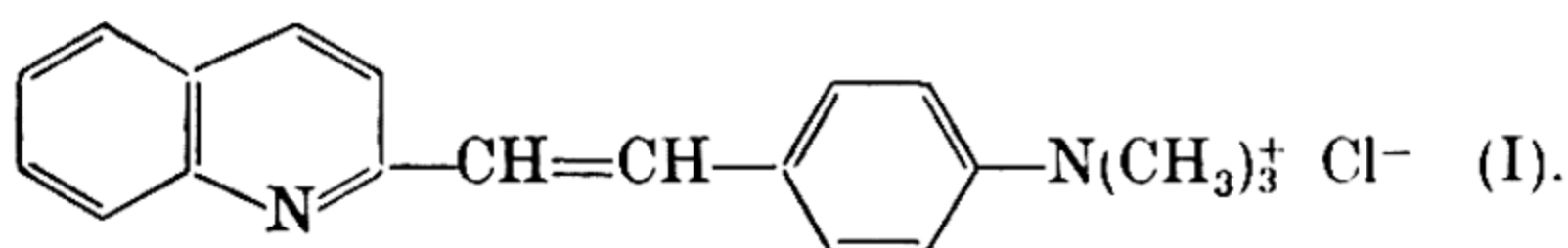
Molecule, having resonance in benzene ring and in NO_2 group



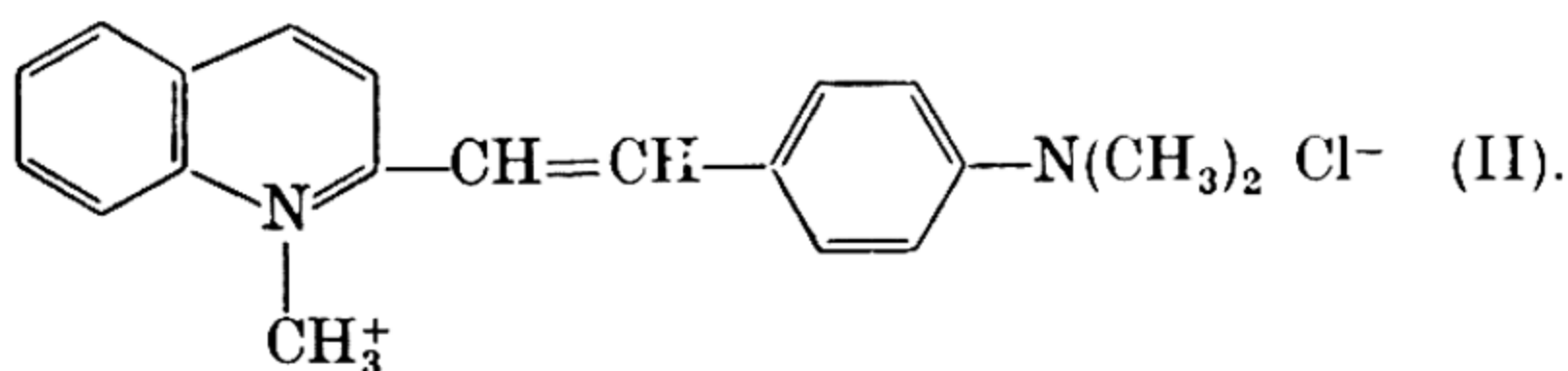
Ion, having increased resonance by charge shift

Inspection of the 'valency formulae' of the dye types on p. 128 shows that they all have many resonance possibilities between hypothetical chemical structures obtained by changing round double and single bonds and moving charges about.

An interesting comparison between the two modes of treatment, 'molecular orbital' and 'resonance' methods, is found in the pair of compounds:



and



Compound I absorbs only in the ultra-violet, while compound II is highly coloured in the visible. On the 'resonance'

band, and again in the plane of the rings. The fluorescence emitted is the same radiation as from 4,950 Å excitation, and

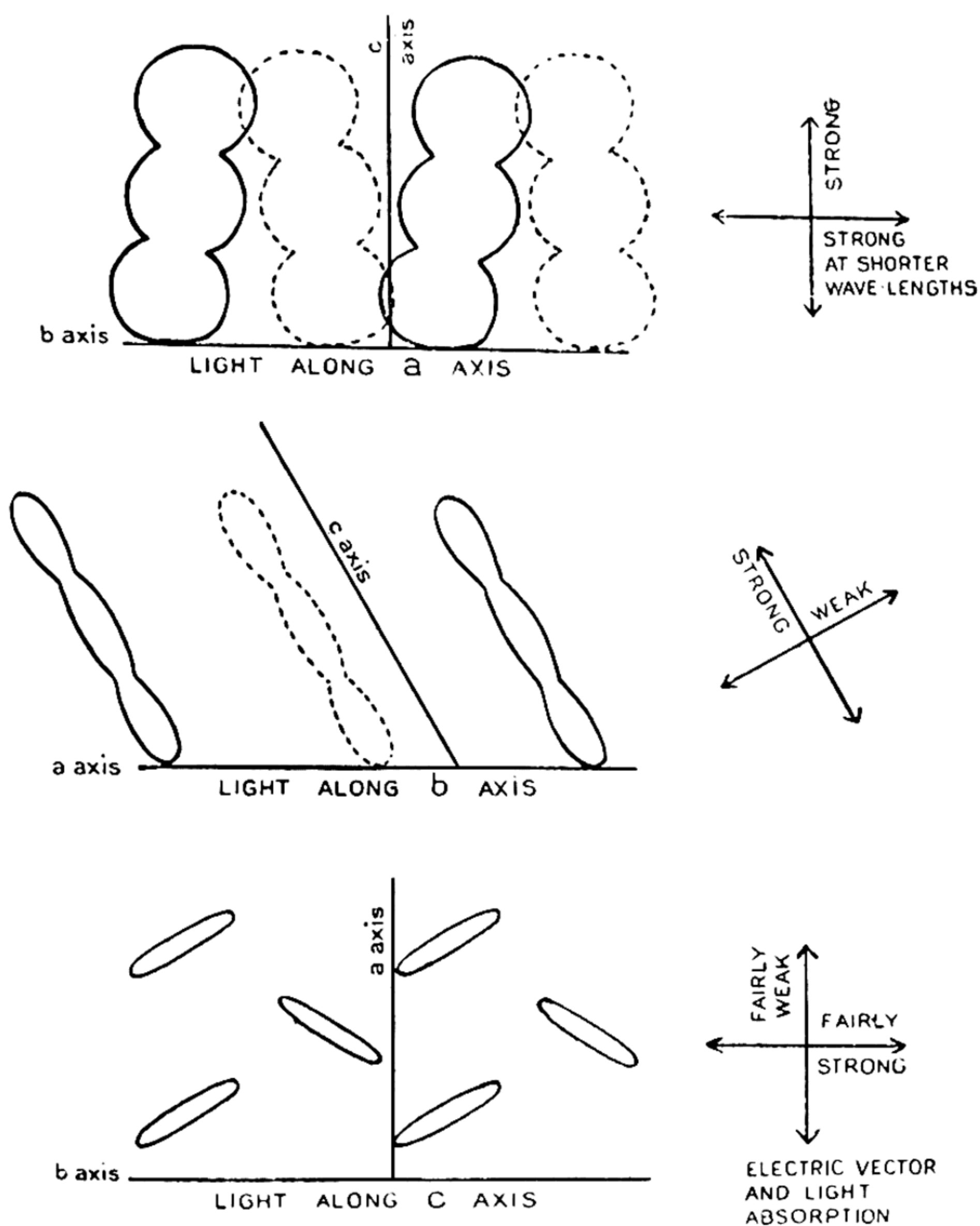
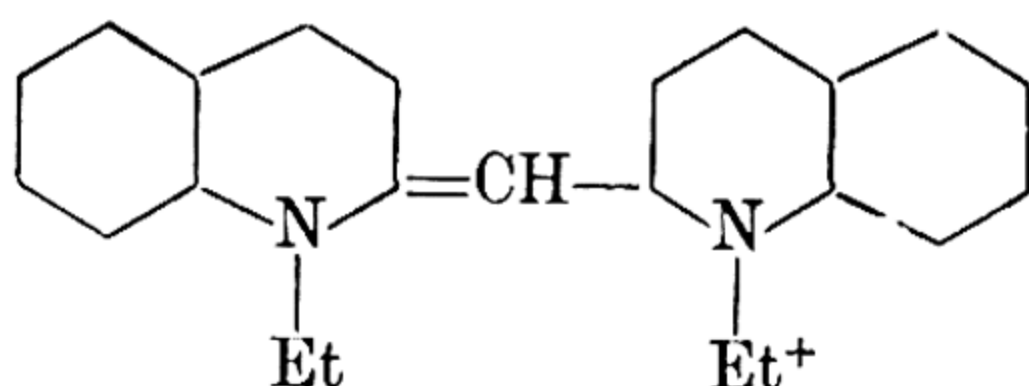


FIG. 39. Dichroism of a crystal containing flat molecules, e.g. anthracene, to plane-polarized light entering normal to the plane of the paper.

is hence 'negatively polarized' (vectors of exciting and emitted light at 90°), being evidently preceded by an electronic change over from the higher to the lower excited level.

The polarization of the fluorescence also varies with concentration and wave-length simultaneously. Dyes often form dimers or larger aggregates at high concentration, (p. 167), and the phenomena shown by uranine can be associated with dimer formation which produces a new band at 4,710 Å in stronger solutions. The most remarkable changes of absorption and fluorescence spectra with concentration are shown by pseudoisocyanine,



The alcoholic solution shows an absorption band at 5,250 Å, the dye being in the monomolecular state. Dilute aqueous solutions absorb at about 4,850 Å, the dye being in a dimeric state. Experiments on the same dye oriented on crystal faces show that the monomer band corresponds to absorption of light polarized with electric vector in the plane of the molecule and along its axis, i.e. to the development of a new orbital node (p. 111) on excitation normal to this axis ('*x*' band). The dimer band corresponds to absorption of light polarized with electric vector along the shorter axis in the molecular plane ('*y*' band). The structure of the dimer is unknown. In very strong aqueous solutions filamentous polymers are formed by the action of van der Waals forces causing the molecules to stack together like piles of coins. A new absorption band appears at 5,730 Å polarized with vector along the filament axis, i.e. normal to the molecular plane ('*z*' band). We are thus able to observe the light absorption of the molecule along three mutually perpendicular directions in space. The polymer band is very narrow, and is accompanied by a strong fluorescence having the peculiarity of practically coinciding with the absorption band. These facts show that although the filamentous polymer is held together

by van der Waals forces (probably by intercalation of water molecules) there must be electronic interaction of the π electrons in a direction normal to the molecular planes all down the filament axis, so that the whole colloidal particle behaves as a conjugated molecule to electronic excitation along the filament axis ('z' direction). In agreement with this

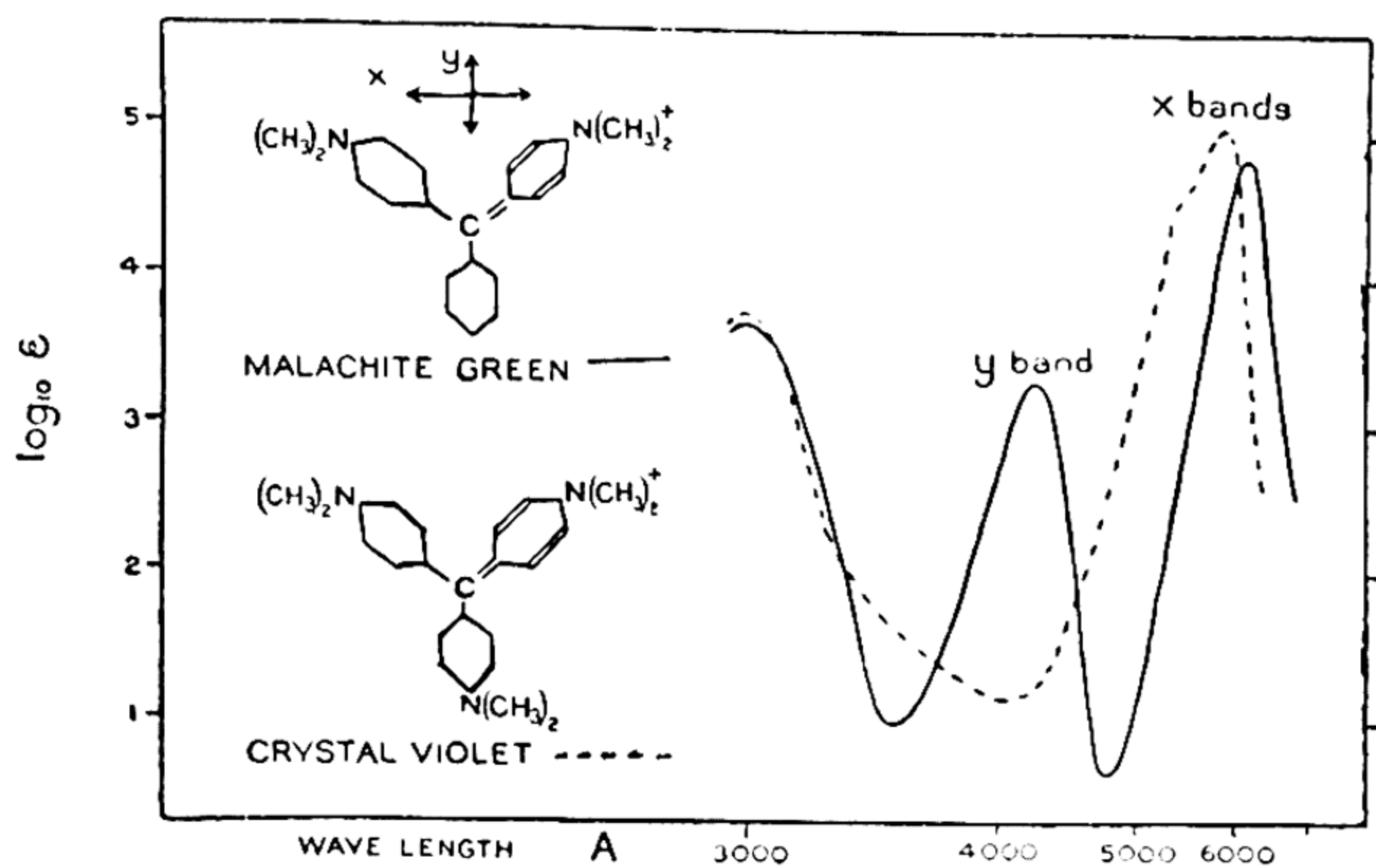


FIG. 40. Absorption spectra of dyes illustrating directive effect in the molecule.

it is found that the fluorescence is quenched by exceedingly low concentrations of suitable substances, under conditions where one or very few collisions of the quencher with a colloid particle removes the energy from any part; the dye particle behaving as a single optical unit. Similar but less well marked and investigated phenomena are found with other dyes. Thionine and methylene blue show monomer absorption at 5,970 and 6,565 Å respectively, and in stronger aqueous solution dimer absorptions at 5,570 and 6,000 Å become more pronounced. The two dye ions, crystal violet and malachite green (Fig. 40), offer a very instructive comparison. The former is symmetrical; it has a strong absorption band at 5,900 Å and another in the ultra-violet at

almost double the frequency. x and y directions are indistinguishable in this ion, and the two bands represent electron transitions from the upper filled orbital to two higher orbitals almost equal energy distances apart. The latter is unsymmetrical, and shows *two* bands in the visible, an x band at 6,250 Å and a y band at 4,230 Å, as well as an ultra-violet band. On the *resonance* concept it might appear that crystal violet should absorb at longer wave-lengths than malachite green; evidently it is not the 'total resonance' which must be considered, but the 'resonance' along the long and short directions of the molecule.

The colours of the ions of the *transitional elements* are due to the fact that these substances have *incompletely filled* sets of $3d$ orbitals. The electrons can be allotted in several ways among the five possible d orbitals so that there are a number of atomic levels of small energy differences; transitions from the lowest to neighbouring ones occur by absorption in the visible region.

TABLE 2

<i>Ions</i>	<i>Number of d electrons</i>	<i>Ions</i>	<i>Number of d electrons</i>
V ⁺⁺⁺⁺ (blue)	1	Fe ⁺⁺ (pale green)	6
V ⁺⁺⁺ (green)	2	Co ⁺⁺⁺ (red, etc.)	
V ⁺⁺ (lavender)	3	Co ⁺⁺ (pink or blue)	7
Cr ⁺⁺⁺ (violet or green)		Ni ⁺⁺ (green)	8
Mn ⁺⁺⁺ (violet, etc.)	4	Cu ⁺⁺ (blue)	9
Cr ⁺⁺ (colourless)		Cu ⁺ , Zn ⁺⁺ (colourless)	10
Mn ⁺⁺ (pale pink)	5		
Fe ⁺⁺⁺ (pale yellow)			

Scandium and titanium ions are also coloured by $3p \rightarrow 3d$ orbital changes which occur with rather small energy absorptions. All the above absorptions are relatively feeble, being practically 'forbidden' transitions. They are strengthened through increase of the transition moment, and slightly altered in position, when the ion forms hydrates, ammines, and other complexes. Anhydrous copper sulphate, for

example, is white, the monohydrate pale blue, the normal hydrate blue, and the ammine deep blue. Cobalt ions Co^{++} in solution are pink; when caused to form the complex CoCl_4^- as happens in the crystalline double chloride of caesium and cobalt they appear blue. The colour of nickel and cobalt dissolved in glasses depends on whether the element exists as an interstitial ion or is connected with the oxygen valency network of the glass; though the wave-length changes, the fundamental nature of the absorption as an inter- $3d$ orbital transition is unaffected. The absorption of chromates, permanganates, and similar coloured anions of transitional elements may also be ascribed to the same cause which gives colour to the corresponding cation, modified in strength and wave-length by the associated oxygen atoms.

The rare-earth ions also absorb in the visible region and are characterized by complicated spectra and very narrow absorption bands. The transitions involved are between orbitals of the unfilled $4f$ group. The visible colours of the trivalent ions are given in Table III.

TABLE III

<i>Trivalent ion of</i>	<i>Colour</i>	<i>Trivalent ion of</i>	<i>Colour</i>
Pr	Green	Tb	Almost colourless
Nd	Red-violet	Dy	Yellow
Il	Yellow-green	Ho	Yellow
Sm	Yellow	Er	Rose
Eu	Almost colourless	Tu	Green
Gd	Colourless	Yb	Colourless

These ions contain 2–13 electrons in $4f$ orbitals. The deepest colour centres on the ions having the f orbitals either about $\frac{1}{4}$ or $\frac{3}{4}$ filled. The absorption of all the inorganic ions is very directive, depending on the orientation of the electric vector of the incident light on the ions. Crystals containing these ions are therefore often markedly dichroic (p. 39 and Fig. 39).

Another type of absorption by inorganic substances,

characterized by very great intensity, is shown by certain crystals containing adjacent ions in different valency states. The best-known example is Prussian blue, represented by $\text{KFeFe}(\text{CN})_6$. The iron atoms are arranged in the crystal alternately in the ferrous and ferric state. The 'ferric' ions are surrounded cubically by six coordinated CN groups; because of the three-dimensional extension of the crystal the 'ferrous' ions also find themselves spatially surrounded by six CN groups from neighbouring complexes. The intense and long-wave light absorption may be attributed to an easy electron transference from 'ferrous' to 'ferric' ions within the crystal lattice resulting in a change of their functions. The coloured substances molybdenum blue and tungsten bronze, which are oxides with the metal atoms in two valency states, made by partial reduction of the higher oxide, behave similarly. There is also the peculiar black double chloride of caesium and gold which has been shown by X-ray analysis to have a structure of caesium ions, AuCl_2^- (aurous) and AuCl_4^- (auric) ions for whose light absorption a similar electronic shift may be assumed. The intensity of the absorption must be caused by a large transition moment and the process somewhat resembles the absorption by a metal itself. Another interesting substance is $\text{K}_4\text{Mn}(\text{CN})_6$ whose molecules are pale yellow in solution but which forms dark blue crystals probably having manganese atoms in two valency states.

The exact nature of the transitions involved in many inorganic substances on absorbing light has at present rarely been worked out. The oxygen molecule is peculiarly interesting. Each atom has six electrons and four participate in links. The bonding in the molecule may be regarded as built up of a pair of electrons forming an essentially σ_g bond by overlap of two $2p$ orbitals in line, two pairs of electrons in π_u orbitals at right angles to each other, as in the acetylene molecule, while the last two are non-spin-paired in two anti-bonding π_g orbitals at right angles (since no more bonding

orbitals are available). The molecule only differs from a true diradical in that the uncoupled electrons have parallel instead of independent spins. The ground level is thus a triplet state (p. 91) and the molecule absorbs at relatively long wave-lengths. The linkages in molecules such as Cl_2O or ClO_2 , or an ion like MnO_4^- , for example, are not so easily treated by the above approximate methods which are used for carbon compounds, and it is often uncertain whether a 'valency' electron is excited or not, even on the simplifying assumption that the electrons can be divided between 'bonding' and 'non-bonding' orbitals. An interesting simple comparison is found by analysis of the spectra of sodium and magnesium diatomic hydrides. Table IV shows the molecular data obtained:

TABLE IV

Molecule	Radius A		Vibration frequency cm.^{-1}	
	Ground state	Upper level	Ground state	Upper level
NaH	1.88	3.03	1170.8	335.2
MgH	1.73	1.70	1493	1603
MgH^+	—	2.02	—	1138.4

In sodium hydride the molecule greatly lengthens on excitation, and its vibration frequency drops, indicating a weakening of the bond through the excitation (to an anti-bonding orbital) of one of the *valency* electrons. The MgH molecule does not show this effect; evidently the electron excited in the observed spectra is not a valency one. Excitation of the *ionized* molecule MgH^+ , however, does weaken the link, showing that the second electron here affected is from the Mg—H link.

The visible absorption bands of chlorine are of interest owing to the photochemical behaviour of the molecule (pp. 92 and 206). Of the 14 outer electrons of Cl_2 , two pairs are in practically 'non-bonding' (i.e. almost 'atomic') orbitals. In the ground state one pair of the remainder form the major

part of the link in a σ_g orbital, two pairs are in two π_u orbitals with nodal planes at right angles, and two pairs are in two 'antibonding' π_g orbitals. The electronic transition on light absorption may be written:

$$\sigma_g^2 \pi_u^4 \pi_g^4 ({}^1\Sigma_g^+) \rightarrow \sigma_g^2 \pi_u^4 \pi_g^3 \sigma_u ({}^3\Pi_u, {}^1\Pi_u),$$

i.e. one electron passes from a π_g orbital to another antibonding one σ_u , giving two excited levels, a triplet and a singlet, depending on whether the spins are similar or opposite.

Absorption of Condensed States

The absorption spectra of the liquid and solid forms of substances with well-defined molecules generally closely resemble those of the gas, except that all rotational and much of the vibrational structure is obliterated by molecular distortions due to thermal energy destroying the sharpness of levels. The sharpness is increased if the optically excited electron comes from some way down in the atom, and not from the outermost shell, as with manganese, chromium, and uranyl salts, and still more with rare earth salts, which show quite fine lines on absorption, owing to the small interaction of the transitions with lattice vibrations. Extremely low temperatures increase the structure observable in the spectra of condensed substances. In most cases it is found that the effect of changing from vapour to a dissolved state, or of increasing the dielectric constant of the solvent, of an absorbing substance is to cause the absorption curve to move towards the longer wave-lengths. This is because the solvent attracts and electronically disturbs the dissolved molecules (with consequent lowering of level by the amount of the interaction energy), having a greater effect upon the *higher* than upon the *lower* level of the substance. The magnitude of the effect depends upon the polarizability of the molecular level and the forces the solvent can exert. It is particularly well shown in the absorption (and fluorescence) spectra

of dimethylnaphtheturhodine dissolved in hexane, benzene, ether, alcohol, etc., which move from the green region to the red as the dielectric constant of the solvent is increased. Sometimes a solvent may exert a large effect by increasing the degree to which a transition is *permitted*, so that the extinction coefficients of the solution are much greater than those of the gas (e.g. bromine as gas or solution).

Where the *solid* state is concerned there are two modes of approach to the problem, each an idealized conception and representing two extreme points of view. In the first place the electrons in the outer atomic shells may be regarded as *localized* in chemical bonds or on separate atoms. Solid methane, or diamond, approximates to this model. The other mode regards all the outer electrons as 'pooled' in the solid, and it is found that the properties of metals are much more readily understood on this basis. The development of the latter idea proceeds by a series of approximations. A metal may be regarded as a lattice of positive ions in which electrons are embedded. It has already been pointed out that electrons in a box can assume only certain energy levels, depending on the size of the box. Neglecting, then, the effect of the positive ions we arrive at the same conclusion for a metal. A fixed series of energy states exists into which electrons can 'go'. These depend on the size of the crystal—increasing it increases both the number of states and the number of electrons. For crystal sizes well above atomic dimensions the number and density of states becomes so large that for practical purposes the energy of the electron can vary continuously. By an extension of the Pauli principle, no more than two electrons can occupy any one state. Thus even at the absolute zero the electrons will have energy, since the states will be filled by pairs of electrons up to a certain energy value, which may be as high as 23 kilo-calories per gram-atom of metal. The above theory takes no account of the influence of the positive ions of the lattice. Their effect is to

change the electric field in which the electrons move from one of uniform potential to one of periodic potential, the period being that of the lattice distance. This has an important consequence on the distribution of allowed energy states. In the neighbourhood of values of electron momentum $mv = h/\lambda$, when the wave-length λ becomes comparable to the lattice distance, it can be shown mathematically that a band of energies between certain fixed limits is forbidden. The limits vary with the *direction* of the electron in the crystal. Energy states form an allowed band up to a certain value, then there is a blank region, followed by another band of states, with further bands and gaps at still higher energies. In univalent metals it appears that the lowest band is not filled—there are more states than pairs of electrons. When an electric field is applied to the metal, electrons are forced to vacant higher states in the band, gaining energy and moving in the field. So can be explained the high electrical conductivity of a metal. It diminishes with rise of temperature because the electron waves are increasingly scattered by the thermal vibrations of the positive ions. Impurities similarly act as scatterers. In other metals, where the lowest band is filled, it is overlapped by the next highest band, i.e. there is no gap between the bands, so that electrons can pass to higher levels. On the basis of these ideas an understanding of many of the properties of metals—conductivity, ductility, thermoelectric behaviour—and alloy formation is obtained, and a semi-quantitative mathematical treatment of the optical properties of metals becomes possible.

The typical *insulator*, e.g. solid salts, silica, and organic compounds, has its lowest energy band of levels exactly filled with electrons, with a wide gap between it and the next level. It is incapable therefore of conducting an electric current, and an explanation is afforded of the enormously large factor, about 10^{24} , between the electrical conductivity of silver on the one hand and quartz on the other. The light-absorption

bands of an insulator are treated from two points of view. If we take the over-simplified picture of the solid as consisting of atoms or molecules with little electronic interaction we see why, in some cases, the energy levels of the gaseous and solid forms are little different, the latter being merely broadened by crystal forces (e.g. organic compounds). A *salt*, however, has strong interionic forces. The absorption may be due to the anion, as in alkali and many other halides and sulphides, or to the cation, as in such cases as copper, chromium, nickel, or cobalt, etc. The energy bands of the crystal and of the corresponding gaseous constituent ion are now so different that it may be difficult to correlate the two. In some examples, however, experimental evidence may be found to identify the type of electronic change associated with particular absorption bands. From the 'pooled electron' concept the absorption of light by an atom, ion, or molecule in a crystal moves an electron to a higher level, and leaves behind a 'positive hole'. At high excitation energies the electron passes into an unfilled band (the conductance band) and the crystal becomes 'photoconducting'. Both the electron and the positive hole are mobile.† This is the inner photoelectric effect. (At very much higher energies the electrons may be able to leave the metal surface, overcoming the potential difference there. Chap. X—*outer* photoelectric effect.) With the absorption of smaller quanta the electron does not escape from the field of the positive hole, and in which it can take up energy levels similar, in a simple case, to those round an atomic core in a free atom. This association of electron + positive hole is called an 'exciton', and it can be shown to be mobile. We can thus understand the experimental facts that absorption of light by a crystal is closely analogous to that of its gaseous constituents, with

† Actually photoconductivity is found at lower energies of excitation, and as it is more marked with imperfect crystals it is concluded that the photoelectrons arise from absorption at cracks where the energy levels are lower.

the addition of change of energy values of the levels and their broadening by lattice vibrations. The spectral structure is sharpened by lowering the temperature. From the viewpoint of the chemist, the free electrons + positive holes become ions or molecules in varying states of excitation (up to ionization), and the mobility of positive holes or of excitons is translated as the handing on of excitation energy from unit to unit in the crystal structure.

To complete this survey of newer modes of looking at crystals, semi-conductors and the effects of impurities on insulators may be mentioned. If the gap between the lowest and the next band of permitted energy levels is very small, some electrons may jump into the higher band and become 'conduction electrons' by thermal energy. The same effect may be produced by impurities which have energy states lying in a gap of those of the bulk substance. In these crystals there will be a small electrical conductivity which *increases* with temperature, e.g. selenium or cuprous oxide. The absorption of light by similar systems is discussed later in connexion with photocells and problems of phosphorescence.

IV

THE TRANSFORMATION OF ABSORBED RADIATION

WHEN light is absorbed by a substance its energy may be transformed in various ways. It may be re-emitted as

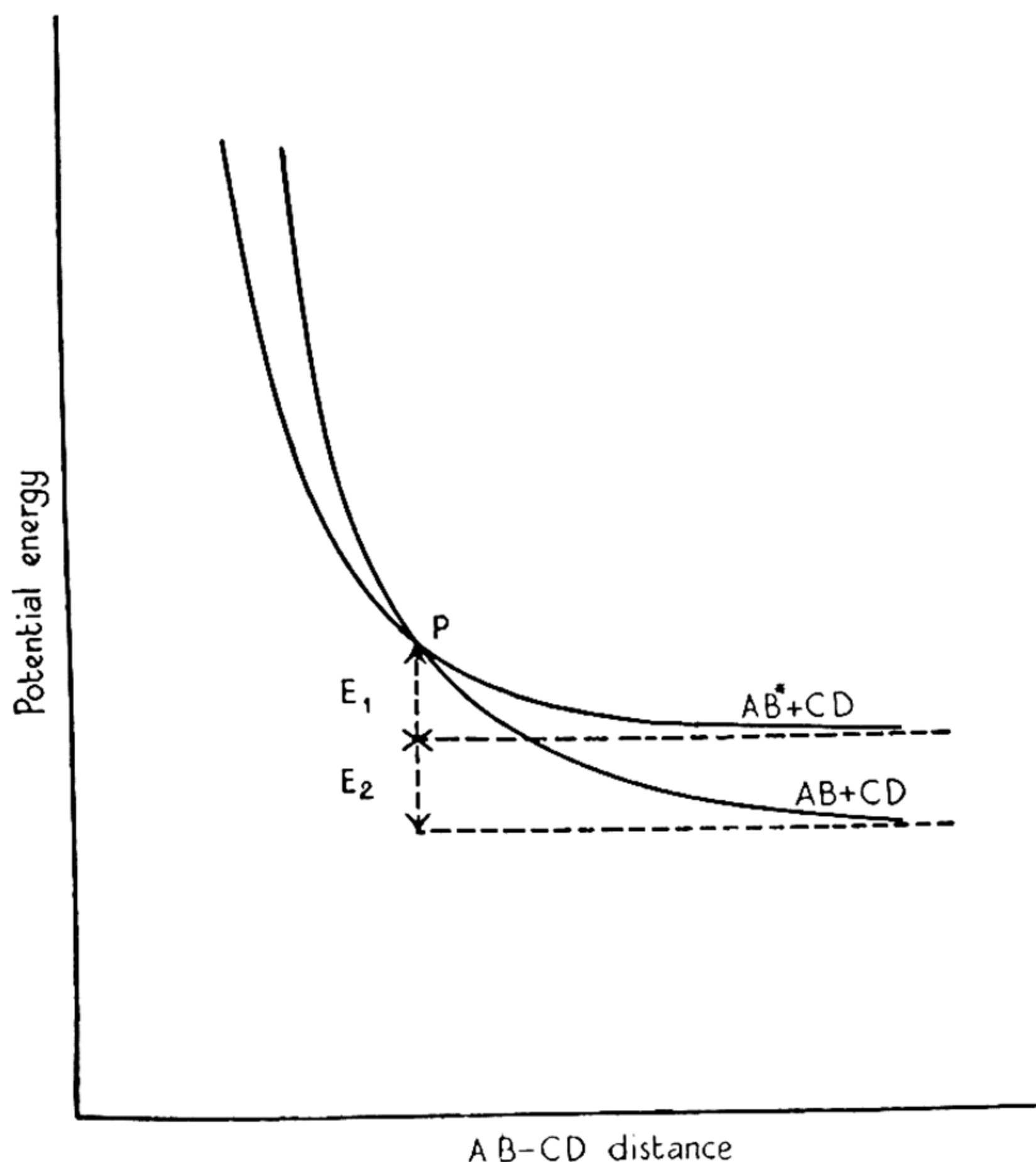


FIG. 41

resonance or fluorescence radiation; the excited molecule may enter into chemical reaction or may dissociate; or the electronic energy may be degraded by collisional or other processes into heat-energy. Chemical and dissociation processes are considered later. The conversion into heat may

be visualized by means of potential energy curves. Imagine an excited diatomic molecule AB^* colliding with another molecule CD . They repel at all distances, and the potential-energy-distance diagram of the system $AB^* + CD$ (treating the molecules as atoms for simplicity) has the form shown

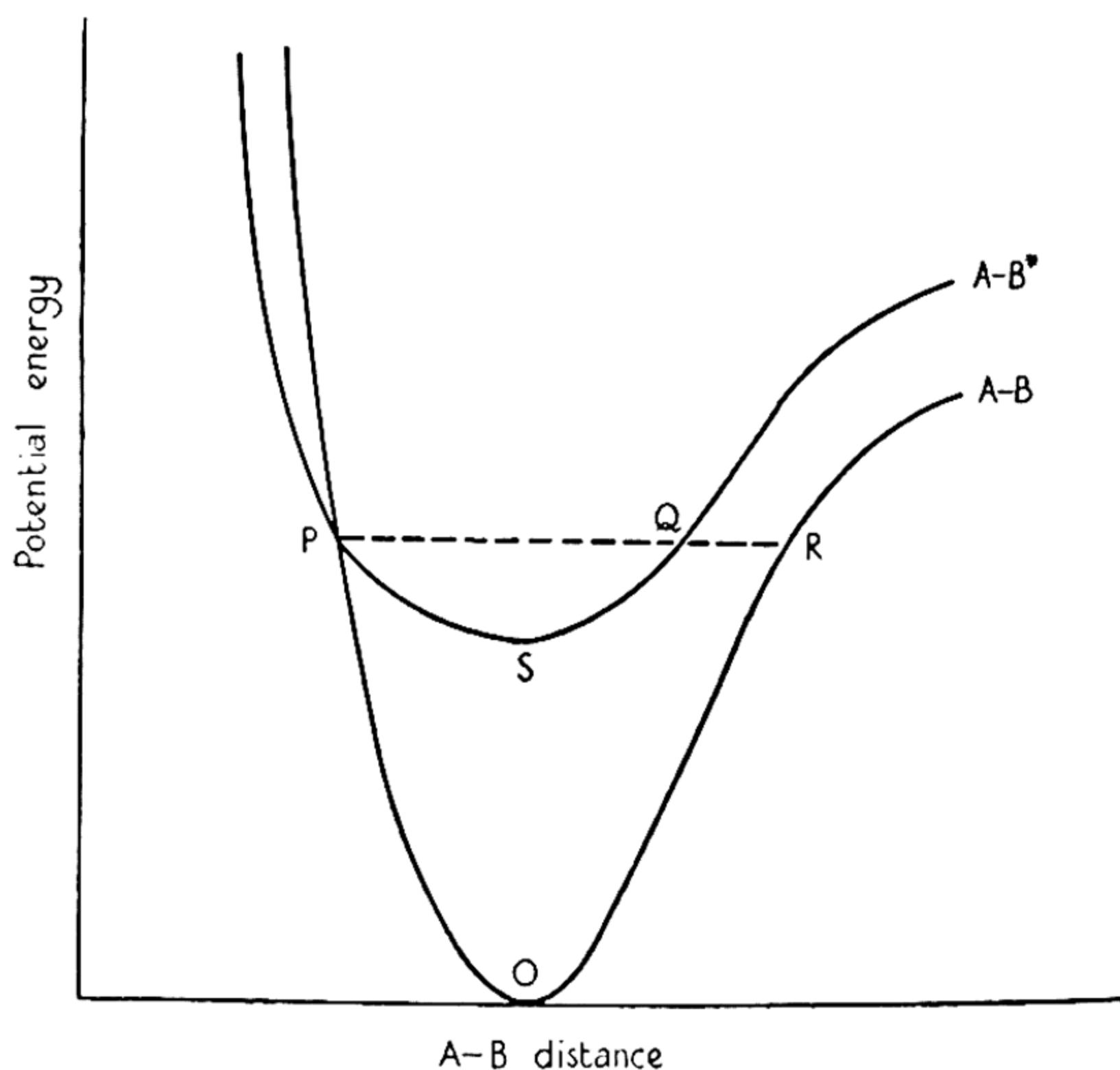


FIG. 42

by the higher curve on the right-hand side of Fig. 41. If the molecules impinge with enough energy E_1 to cause them to reach the point P , the system may change to the other curve, and the two molecules may separate as unexcited AB and CD with excess translational energy E_2 . Alternatively the energy may be taken up by CD partly or wholly as electronic, vibrational, or rotational energy; processes not so easily shown on a potential energy diagram. The behaviour of a frictionless marble rolling in the curves illustrates the processes occurring. Another type of deactivation of an internal as contrasted with the above external nature is shown in Fig. 42. The potential-energy-distance curves of the atoms

in the molecules AB^* and AB are assumed to cross at P . An excited molecule, normally represented by a point near S , may pass to higher vibration levels near P by chance thermal processes. It may then change from vibrating along PQ to the line PR , and become a highly vibrating form of the ground level AB . The vibration energy rapidly comes into equilibrium with rotational and translational energies by collisions with other molecules. Internal deactivation is clearly much more probable in polyatomic molecules where the simple curves are replaced by complex hyper-surfaces. The degradation of electronic energy in solids may be represented similarly to Figs. 41 and 42, if the abscissae of the curves are replaced by lattice distances (energy being degraded into vibrations), and in liquids by regarding them either from the gaseous or the solid point of view, since the distinction here between vibrational and translational energy cannot be maintained clearly.

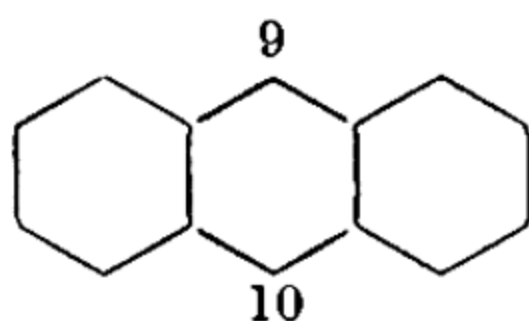
Important information about the nature of collisional processes has been obtained in a variety of ways. One type of experiment consists in exciting sodium atoms, for example, by light in presence of other atoms which have energy-level differences near to differences between sodium levels. Under these conditions the foreign atoms freely take up energy from the excited sodium atoms and emit their own characteristic lines. Another experimental method is to investigate the quenching of the emission spectra of sodium atoms or iodine molecules excited by light when other molecules are added. The degree of quenching varies both with the nature of the added gas and with the actual levels to which the sodium or iodine is excited, or rather with the relation of these levels (electronic, vibrational, or rotational) to those of the added molecules. In the actual performance of these experiments care must be taken to use as exciting light a sufficiently monochromatic source, since ordinary sources are wider than the absorption lines of the substances, and these lines are

broadened by the added gas, altering the amount of light absorbed unless the above precaution is taken. Work along these lines has established the following generalizations: energy changes on collisions are most probable when there is approximate resonance between the colliding bodies, i.e. when electronic energy is transferred mostly as electronic energy, vibrational energy as vibrational, or rotational as rotational, the amount of kinetic energy liberated in each step being as low as possible. Rotational changes are more readily produced than vibrational changes, and collisions rarely change the vibrational quantum numbers by more than one unit at a time. The selection rules which hold for spontaneous transitions are not closely obeyed, though they commonly indicate the most likely changes. The extent to which energy is transferred on collision is largely dependent on the amount of electronic interaction between the molecules or atoms. It thus appears that energy degradation on collision to heat is a stepwise process occurring in a large number of stages. These results are practically what would be expected if the systems are regarded as vibrators obeying the laws of ordinary dynamics; collisions between such bodies being 'elastic' if they have no internal frequencies in common, but 'inelastic' and involving energy transference if there is approximate coincidence of frequencies. Inelastic collisions are often termed 'collisions of the second kind'. In degradation processes electronic energy is often transferred from one molecule to another over distances several times larger than those of ordinary 'molecular diameters' which are obtained from experiments on the transfer of momentum on collision. This effect is marked where the molecules have approximately equal energy-level differences.

The alternative to the degradation processes discussed above is that an atom or molecule may lose its energy by radiation. Atoms or simple molecules can rarely resist for long the deactivating influence of collisions. The mean life

of an undisturbed excited particle is usually about 10^{-8} seconds. The life may be much longer if the excited level is one which cannot return directly to a lower state because of the selection rules. If it suffers a collision within this time interval it is exposed to the chance of deactivation. In a gas at 760 mm. pressure the interval between collisions is about 10^{-10} seconds. Consequently emission of radiation from simple particles is not often observed at gas pressures above 10 mm.

There are certain types of complex molecules, however, which are peculiarly resistant to deactivation. In these the electrons concerned in the excited levels seem to be shielded from external influences. They re-emit light, after being excited, as *fluorescence radiation*, even in the dissolved or solid state where collisions are much more frequent than in a gas. However, they show a variation of behaviour under different conditions, indicating that deactivating influences, external or internal, occur when the molecule is suitably affected by its environment. Among inorganic substances the uranyl salts and the platinocyanides are strongly fluorescent in the crystalline state; much less so when dissolved. The trivalent ions of Eu, Dy, Sm, and Tb are also fluorescent, in the crystalline state, in solution, and in 'didymium glass', as well as in some specimens of fluor spar. Organic substances of aromatic structure, such as benzene and anthracene, and particularly molecules containing the ring system,



where the atoms of the ring at positions marked 9 and 10 may be CH, O, N, or S, show fluorescent properties in solution and sometimes in the solid state. The fluorescent dyes mostly belong to this class; they are, however, rarely fluorescent in the solid state. Fluorescence in organic compounds is always associated with 'non-localized' molecular orbitals

of conjugated substances. Changes among such orbitals (cf. Figs. 31 and 32) do not disturb the atomic framework much, so that the potential energy curves of lower and upper states are nearly parallel and show little tendency to 'cross'. 'Electron attracting' groups, such as —NO_2 or halogens, when introduced into organic compounds, tend to localize electrons within themselves and change the system towards that exemplified by Fig. 42. 'Electron repelling' groups such as —NH_2 usually increase fluorescence efficiency and also cause it to be of longer wave-length by changes qualitatively explicable by simplified potential energy curves.

The relation between scattering, the Raman effect, resonance radiation, and fluorescence is a matter of importance. We may attempt to illustrate these processes by reference to the effect of light on iodine. First let the iodine *atom* be considered. Light of a certain wave-length causes it to pass from its ground level to the first excited level. When the atoms are at so low a pressure that collision intervals are longer than about 10^{-8} seconds, the 'lifetime' of the excited state, the situation may be treated as one of 'free' vibrations of the electronic shell. The atoms take up the light energy, but give it all out again as radiation of the same frequency, scattered in all directions, i.e. resonance radiation (p. 26). If, however, the 'electrical vibrations' are 'damped' by collisions, as when foreign gases are present, the absorbed radiation is converted into heat energy of the atoms (p. 151) and no re-radiation occurs. (Damping is in electromagnetic or wave language the equivalent of absorption and degradation to other forms of energy, normally treated by quantum theory.) Light of other wave-lengths sets the electronic shells of the atoms into forced vibrations in the frequency of the light; they re-emit this light, and the interference between primary and secondary waves produces the phenomenon of dispersion in the gas.

Now we may consider the iodine molecule. This can take

up light over a wide band of wave-lengths in the visible region. Its spectrum is similar to that of chlorine (p. 92). At wave-lengths on the red side of $4,995 \text{ \AA}$ the absorption has a fine structure of rotation lines grouped in vibrational band systems; beyond $4,995 \text{ \AA}$ the spectrum is continuous since the molecule suffers photodissociation. At very high gas pressures all the 'electrical vibrations' (not to be confused with *nuclear* vibrations) induced by absorbed light are 'damped' and no re-radiation occurs as with the 'atom' gas. At lower pressures 'electrical vibrations' from wave-lengths shorter than $4,995 \text{ \AA}$ are still damped, since the energy is converted into energy of separation of the atoms, but when illuminated by light of a lower frequency the molecules pass to excited levels. The molecules receive electronic energy, causing them to pass from the Σ to a Π level (Fig. 22); vibrational and rotational energy changes of the nuclei also occur depending on the particular frequencies absorbed by different molecules. The molecules now re-emit in all directions the light they have taken up and produce their resonance radiation. They not only emit the exact frequency they have absorbed, however, but new frequencies differing from that absorbed by the nuclear vibrational and rotational frequencies of the molecule. Molecules which do this are left in different rotational or vibrational levels from those before they took up the light. Since at the ordinary temperature the bulk of the molecules are in their lowest vibrational level, there is a much greater chance of their gaining a vibrational quantum after the above process than losing one. For rotational level changes the chances are more equal. The resonance radiation thus consists of a spectrum, mostly of longer wave-length than the exciting radiation, composed of a fine structure of lines of frequency difference from the exciting line equal to vibrational and rotational frequencies of the molecule. When the exciting light is not monochromatic it is complex in appearance, but is resolved into separate series

of lines by using light corresponding to one line (of the rotation structure) only in the molecular absorption spectrum.

Molecules of greater complexity than the iodine molecule are subject to so many processes of deactivation (p. 153) that they can rarely be brought to execute 'undamped' free vibrations of their electronic shells. Consequently their resonance spectra cannot be obtained with light which they absorb. If, however, they are illuminated with light which they do *not* absorb, a new sort of scattering appears. In addition to the coherent scattering (p. 25) which produces the phenomena of dispersion, and the Rayleigh scattering (p. 34) due to fluctuation of optical density, in both of which no change of wave-length occurs, there is a very faint emission of the resonance spectrum, called, under these conditions, the Raman effect. Monochromatic illumination is, of course, necessary. The molecules execute 'forced electrical vibrations' of the period of the light, and those that emit them unchanged in frequency merely assist in the dispersion effect. A fraction of the molecules, however, emit light quanta of changed magnitude, since they retain or contribute energy equal to their nuclear rotational or vibrational quanta. As this emission occurs in much shorter time intervals than 10^{-8} seconds, in fact within a period of about 10^{-15} seconds, collisions or other influences have no time to exert a deactivating effect. What is effectively a resonance spectrum is thus obtained; the process, however, not being that of the return of an excited molecule from a stable quantized upper level to the lower vibrational (or rotational) levels of the ground electronic state, but the quick return of a molecule to these levels from a non-quantized unstable distorted state it had momentarily been forced to assume by the passage of the non-absorbed light waves. The Raman spectrum consists of the Rayleigh scattered exciting line and on its long-wave side much fainter lines whose frequency differences from the exciting line correspond to rotational or nuclear vibrational

frequencies of the molecule in its ground state. The rotational lines are usually swallowed up in the heavily exposed Rayleigh line. Raman data therefore supplement infra-red absorption data in providing values of ground state vibrational frequencies. They are specially valuable because the selection principles differ from those for infra-red absorption. For *absorption* to occur there must be a 'dipole transition moment' (p. 123) between the ground and upper levels; consequently symmetrical molecules like H_2 or Cl_2 cannot absorb in the infra-red, since mere change of vibration level produces no change of polarity. Vibrational frequencies of these molecules are only obtainable from Raman spectra; the selection rule for the appearance of a Raman line being that the *polarizability* (p. 29) of the molecule should change with the *phase* of its vibration. Infra-red absorption bands commonly have *P* and *R* branches, corresponding to increases or decreases of rotational quanta by one unit associated with the vibrational transition, and due to the electric vector of the absorbed radiation exerting a twist on the molecule. Raman lines are mostly *Q* branches (p. 83). In polyatomic molecules those nuclear vibrations whose excitation have 'transition moments' appear as infra-red absorption bands, and more symmetrical ones such as that vibration of the benzene molecule where all the atoms move outwards and inwards together appear only as Raman lines; some vibrations are 'permitted' in both spectra and some in neither. The actual assignment of observed frequencies to particular vibration modes in a complex molecule is a difficult matter, and is assisted by the above considerations. Raman lines are often strongly polarized; some, however, show depolarization, and these effects are also of value in elucidating vibrational types.

To understand the difference between the resonance spectrum and the Raman spectrum on the one hand and the fluorescence spectrum on the other, we return to a consideration of the absorption of light (of wave-length longer

than $4,995 \text{ \AA}$) in the structured spectral region of iodine. Under low-pressure conditions we have emission of resonance radiation; and under high pressures this is extinguished by the deactivating influence of collisions. At *intermediate* pressures the molecules are robbed of their excess vibrational energy and still retain their electronic energy. This may be illustrated by Fig. 19. On excitation from the ground vibration level of the lower curve the diatomic molecule passes to the upper electronic state vibrating along levels about 5, 4, 3. Collisions remove the vibrational energy, so that the molecules all assume the 0 level. If now they are not electronically deactivated, they will drop (after about 10^{-8} seconds) to the lower curve to vibration levels near the fourth. The vertical distance is less than that of the excitation, consequently fluorescence spectra lie on the long-wave side of the absorption region, though there is generally an overlap. The fluorescence spectrum (in this simple example) is independent of the frequency of the light absorbed, since whatever point the molecules reach on the upper curve, they all emit from the single level 0. The resonance radiation differs in being attached, as it were, to the exciting frequency, corresponding to the excitation from the 0 level to the upper fourth level followed by transitions back to the lower first, second, and third levels. Raman radiation merely differs from the resonance process in that the quantized upper level is replaced by some lower, indefinite, non-quantized, unstable energy level lying in the region between *G* and *A*.

It is evident from the figure that the vibration band spacing of a fluorescence spectrum gives directly the frequencies of the *normal* molecule; in an absorption spectrum the spacing chiefly relates to frequencies of the *electronically excited* molecule. Emission spectra of molecules (excited in a vacuum tube for example) are more complicated to interpret, as transitions occur from several vibrational levels of the excited state to several of the lower, giving interpenetrating

series of band spacings. The fluorescence processes of polyatomic molecules may also be more complex than the two-dimensional representation of Fig. 19, and more than one upper electronic level may be involved.

It is possible from these ideas of fluorescence to see more clearly what are the conditions under which it will be observed in liquids and solids, where collision frequencies are high. The electron system which acts as the emitter must, as already stated, be 'shielded' from external influences. This means it must not be strongly 'coupled' with the vibrational processes in the condensed phase, i.e. its energy level should be scarcely affected when changes take place in these vibrations. It is found that quinine sulphate, uranyl salts, etc., have their emission quenched by halide ions, the order of effectiveness being $\text{Cl}^- < \text{Br}^- < \text{I}^-$, that of increasing polarizability, or degree to which the ion is distorted by an external field. The ion is affected electronically by the excited molecule, and reciprocally affects it, so that the 'isolation' of the fluorescent electron is destroyed and conversion of its energy into vibrational energy between the ion and the molecule is facilitated. In the same way the introduction of halogen atoms into fluorescent dye-stuff molecules causes a reduction of efficiency of emission—cf. the substances fluorescein, eosin, and erythrosin—the polarizable property of the atom within the molecule bringing about a coupling of the electronic excitation and vibrations. The nitro-group in an aromatic molecule is a very powerful quencher of fluorescence.

Fig. 43 shows the absorption and fluorescence spectra of anthracene in three physical states. The following points should be noted: (a) all the bands move towards the red in changing from gas to solution to crystal; (b) the fluorescence band lies just to the red side of the absorption band with a region of overlap; (c) the fluorescence and absorption bands show approximate 'mirror-image' symmetry; this is not

exact, however, for the vibrational structure spacing of the former relates to the ground level and of the latter to the excited molecule (Cf. Fig. 34).

An explanation of the fact that some substances are more fluorescent in the solid state than in solution, and some the reverse, and of the observation that at low temperatures

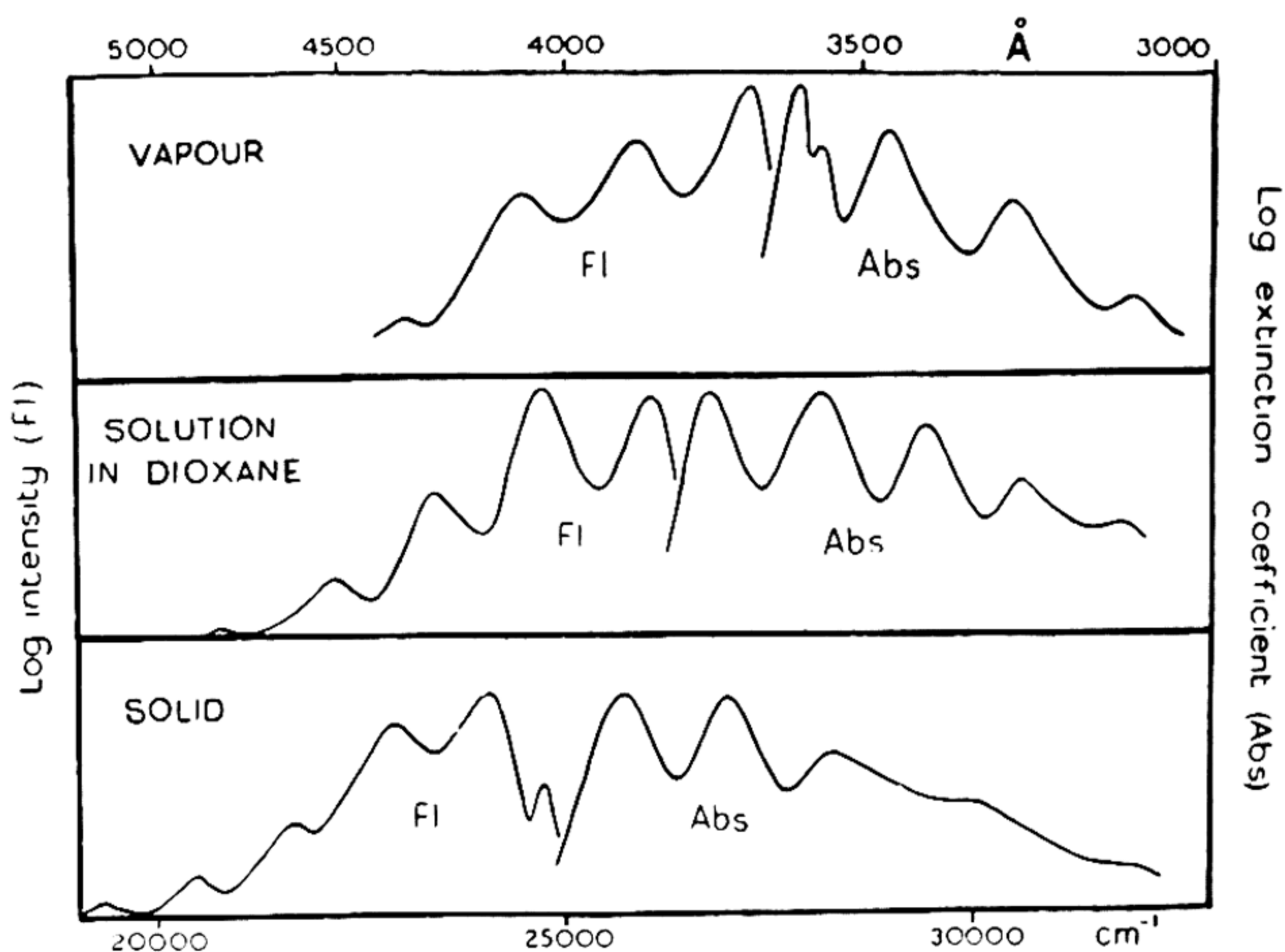
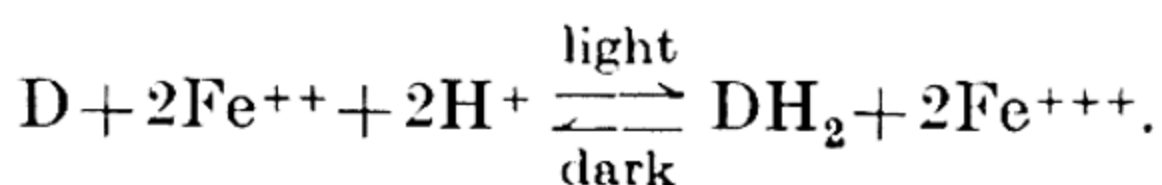


FIG. 43. Absorption and fluorescence curves of anthracene.

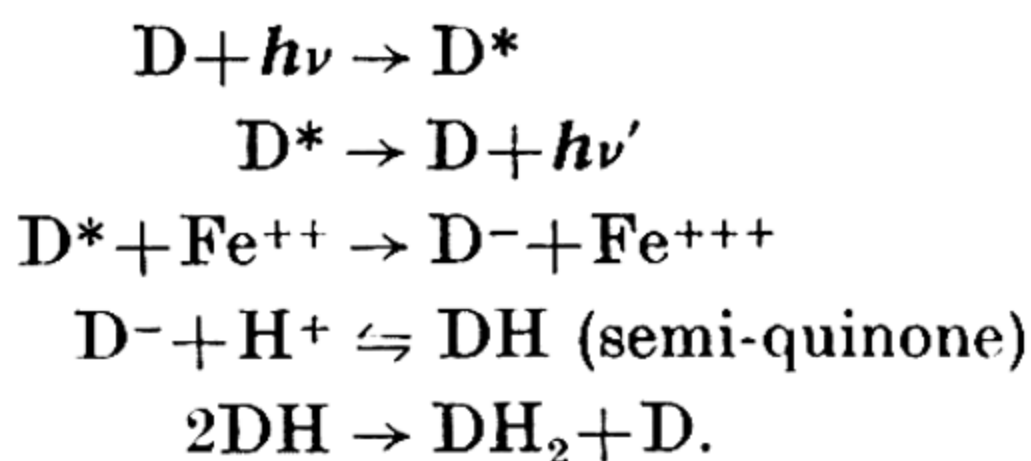
(liquid air) fluorescence becomes a much more common property of condensed phases than at the ordinary temperature, must also be qualitatively sought in terms of 'coupling' mechanisms. The transformations of the electronic energy into vibrational or translational energy as depicted in Figs. 41 and 42 are over-simplified representations for polyatomic molecules because of the use of only two coordinates. The curves should show hypersurfaces of distances plotted against potential energies, and it is not the total value of the latter which is important for quenching, but the effect on that part of the energy associated with the fluorescent centre of the molecule. At the present time we must remain content

with purely qualitative interpretations of the complex state of affairs in actual molecules. We can attempt, however, to distinguish between examples of quenching occurring by intramolecular processes (Fig. 42) and those dependent on collisions (Fig. 41). For example, the fluorescence efficiency of anthracene of about 0.65 scarcely varies in different solvents; it is likely, then, that 35 per cent. of the excited molecules are quenched 'internally'. In common with other aromatic hydrocarbons its fluorescence is strongly quenched by dissolved oxygen. This effect must be collisional. Though peroxides of the form AO_2 , where A = hydrocarbon, are formed in illuminated oxygenated solutions of aromatic hydrocarbons, the quenching of their fluorescence is not wholly due to this reaction, as in many cases it is much greater than can be accounted for by photo-oxidation. The fluorescence of dye-stuffs is not so affected by oxygen, but quenching can be detected, and photo-oxidation also occurs slowly, at a rate greatly dependent on the dye.

An interesting form of quenching is shown by the action of ferrous ions on certain dye solutions, as of thionine or methylene blue. A reversible reduction-oxidation occurs whose net effect is given by

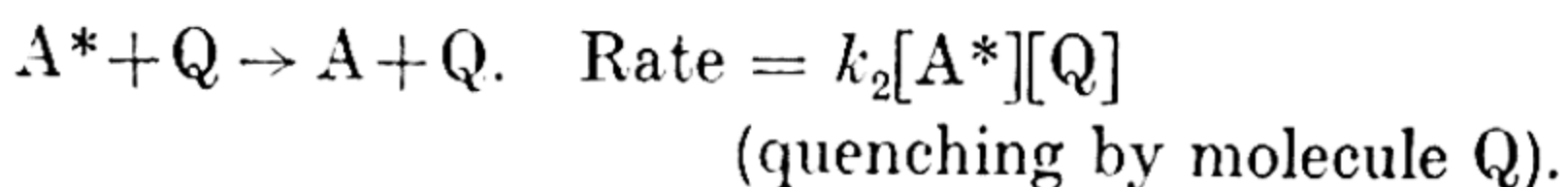
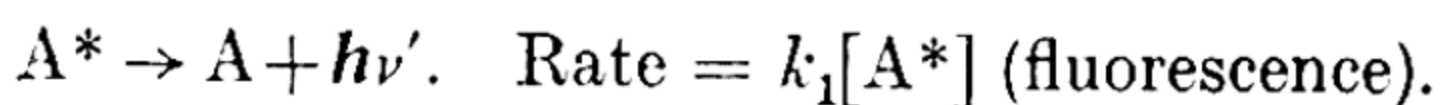


The dye is reduced to the leuco form in light and is oxidized back by a thermal reaction, so that an equilibrium is set up. The vacated orbital of the excited dye molecule is filled by an electron from the Fe^{++} ion, and the complete reaction scheme seems to be as follows:



Solutions of fluorescent dyes often show a complex behaviour when illuminated in presence of oxygen and either oxidizable or reducing substances. They are more photo-reactive than non-fluorescent dyes because the excited molecule D^* is not quickly deactivated, but may live for 10^{-8} seconds, and during its lifetime the possibility of chemical reaction is an alternative to energy loss by fluorescence. Some dyes are reversibly bleached by reducing agents, as above; others by oxidizing agents. The bleaching may be partly or wholly irreversible. In the presence of large quantities of reducing agents and free oxygen the dye may bring about a photosensitized oxidation process of the reducing agent, itself being little changed. Small quantities of reducing agent, however, under similar conditions, often accelerate the photobleaching of the dye itself. Dyes exhibit some or all of these features of photochemical change and the full mechanisms usually remain obscure.

The kinetics of fluorescence quenching in solution have peculiar features which distinguish them from those of ordinary thermal reactions. On the simple mechanism:



it follows that the ratio (Fluorescence of solution without quencher)/(Fluorescence with quencher) $= 1 + \frac{k_2}{k_1}[Q]$, and this equation is usually found to express experimental results. k_1 is the reciprocal of the fluorescence lifetime and is about 10^8 sec.^{-1} . For 50 per cent. quenching $k_2[Q]/k_1$ must be unity, and the following approximate figures may be calculated for a quenching molecule of M.W. about 200 and density about 1.

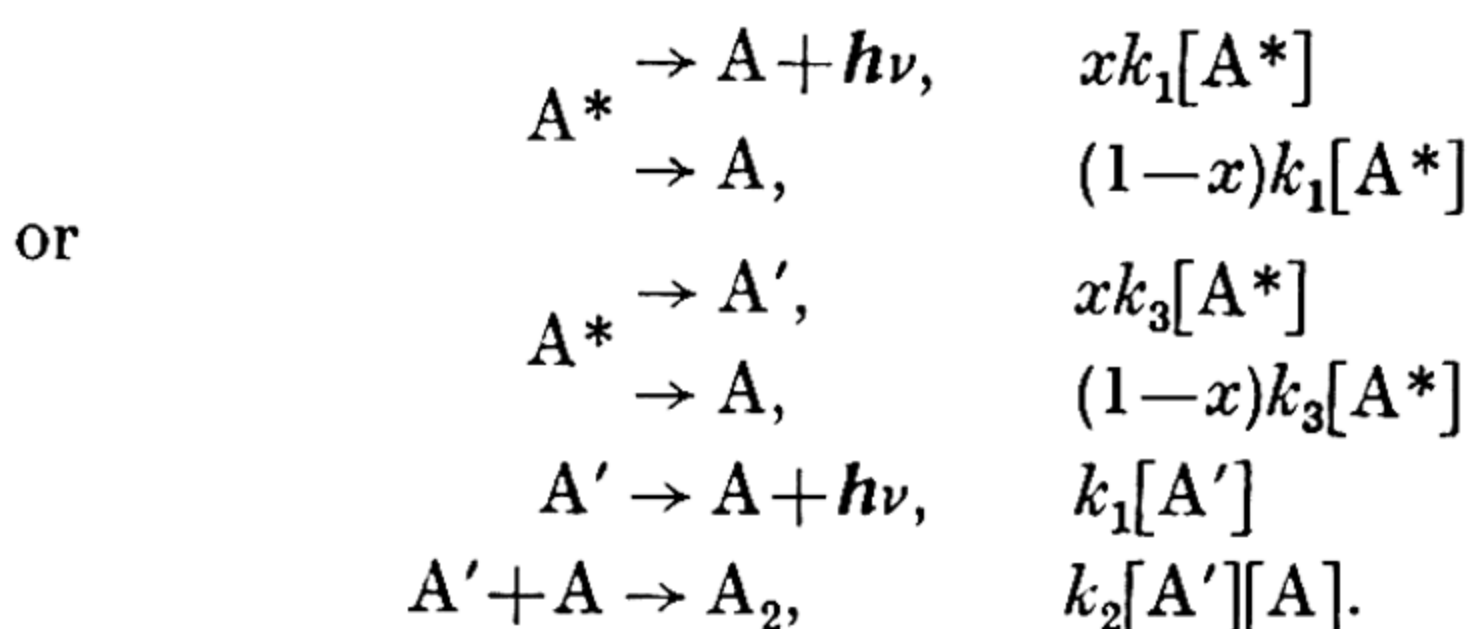
TABLE V

k_2 Sec. ⁻¹ mol. ⁻¹ litre	Concentration of Q for 50 % quenching	Fraction of collisions effective in quenching at zero viscosity
2×10^7	Pure liquid	10^{-5}
10^8	200 gm./l.	5×10^{-4}
10^9	20 gm./l.	10^{-2}
10^{10}	2 gm./l.	10^{-1}
10^{11}	0.2 gm./l.	1

The study of fluorescence quenching therefore affords a means of investigating bimolecular reactions in solution having extremely high constants (10^8 – 10^{11} sec.⁻¹ mol.⁻¹ l.) and occurring at a very high proportion of collisions. Such reactions show a very different kinetic behaviour from bimolecular reactions with ordinarily measurable constants of 10^{-4} – 10^{-1} sec.⁻¹ mol.⁻¹ l. For example, the quenching of the fluorescence of anthracene in solution in various solvents by carbon tetrachloride (k about 10^9) or by dissolved oxygen (k about 10^{10}) increases with rising temperature linearly with increase of fluidity ($= 1/\text{viscosity}$). This indicates that the reaction rate is controlled not by activation energy considerations but by the rate of diffusion of the molecules; when the molecules have come together by diffusion the probability of quenching is high. High viscosity in a liquid does not greatly alter the collision rate between molecules, but increases the proportion of repeated collisions while diminishing those between molecules initially some way apart (p. 214). If the number of collisions required for quenching is small compared with the average number of collisions of repeated kind, the quenching constant will diminish with rising viscosity. In ordinary bimolecular reactions such an effect would be observable only at viscosities as high as those of the vitreous state. A different behaviour is shown in the quenching of the fluorescence of anthracene in solution by bromobenzene. Here the constant is somewhat smaller (about 10^8) and varies

very little between different solvents. Instead of showing the viscosity effect the constant decreases slightly with rising temperature. At the higher concentrations required with this quencher one must suppose that there is always a quenching molecule 'within range' of an anthracene molecule; the small constant being determined by the low efficiency of quenching rather than by the necessities of diffusion. The negative temperature coefficient may be attributed to an orientation requirement between the bromobenzene and anthracene molecules for quenching; the duration of such orientation diminishing with rise of temperature.

Many substances at higher concentrations in solution (or at pressures above low pressures in the gaseous state) show 'self'- or 'concentration'-quenching of their fluorescence. This is shown, for example, by anthracene solutions, and here the quenching is accompanied by photochemical reaction giving dianthracene. In the scheme above we may write A for Q and A₂ for A+Q. Allowance must be made, however, for the fact that in the absence of recognizable quenchers and at low anthracene concentrations the fluorescence efficiency is less than unity. This must be due to either 'spontaneous' or 'solvent' quenching. Two possible modifications of the above scheme are:



For the former the quantum efficiency of A₂ formation is $\frac{k[A]}{1+k[A]}$, where $k = k_2/k_1$, and for the latter, $\frac{xk[A]}{1+k[A]}$, while

the fluorescence efficiency for both is $\frac{x}{1+k[A]}$.

The latter scheme makes the sum Q.E. + F.E. constant = x , and such experimental data as exist support this possibility rather than the other. Self-quenching is observed in other aromatic hydrocarbon solutions, but not in all; e.g. rubrene solutions show it and fluorene solutions do not. Quenching by the halogen compounds mentioned above often leads to photochemical halogenation of the hydrocarbon, but the quantum efficiency does not generally behave as the complement of the fluorescence efficiency. With carbon tetrachloride as a quencher for anthracene in solution photochemical reaction is very marked and may occur at every effective encounter, but no photoreaction is observable with bromobenzene as the quencher. Intermediate degrees of photoreaction are observed with other halogen compounds.

Self-quenching of fluorescence in dye solutions is often well marked (e.g. strong solutions of uranine are non-fluorescent), usually manifesting itself at concentrations above 1 gm. per litre. The effect may partly be due to true quenching processes of the type discussed above. In large part, however, it is not true quenching, but is due to the fact that these substances exist in dimeric and more highly polymerized forms in strong solution; the absorption spectrum is thereby considerably changed, though it overlaps that of the unassociated dye, and the non-fluorescent polymers act as inner filters so that quenching is simulated. As the effect is greater in water than in other solvents it cannot be ascribed to dipole attractions; it is almost certainly due to 'dispersion forces'. London has pointed out that the van der Waals forces holding liquids together comprise permanent dipole attractions, induced dipole attractions, and 'dispersion forces'. The latter play the chief role in liquid formation. An atom or molecule has an electric distribution determined by the square of the amplitude ψ ; it may be symmetrical and have no external field. This quantity,

however, is only a *time average*. The electronic zero-point energy of the molecule produces quickly varying dipoles in the electrical structure which can induce in neighbouring molecules other dipoles in phase and in interaction with the first. An attraction therefore exists where the inadequate treatment based on a neglect of the time variable predicted none. This force is the stronger the lower the characteristic frequencies of the molecule and the greater the 'transition probability' to higher states, i.e. roughly, the greater the extinction coefficient. Both these conditions hold for dye molecules, which may therefore be expected to show peculiarly strong intermolecular attractive forces in solution. The 'polymers' are non-fluorescent presumably because of a greater chance of internal degradation of the electronic energy. Polymer formation, and therefore quenching, is increased by the addition of electrolytes to the solution, this effect being distinguishable from ordinary quenching by added substances, by its dependence on the dye concentration. The non-fluorescence of most dyes in the solid state at ordinary temperature may be ascribed to similar quenching processes arising from the parallel arrangement of the molecules in the crystal.

Some dyes (e.g. benzoflavin in water) show a lengthened period between absorption and emission (10^{-2} sec. instead of the usual 10^{-8} sec.) at certain concentrations. This is associated with dimer or polymer formation in which the excitation energy, by passing to and fro, remains for a much longer period on the molecule before 'deciding' to leave as fluorescence. During this lengthened period there is an increased risk of deactivation by various processes, internal or external to the molecule. In particular, the quenching effect of dissolved oxygen is very marked, occurring at most minute concentrations, while much higher oxygen concentrations are necessary to exert any effect on the short duration fluorescence of the unimolecular dye molecule. For this

reason the long-duration fluorescence remained unnoticed by earlier investigators.

Even in the absence of any of the above effects the *observable* fluorescence from a solution is affected at high concentrations, especially where the exciting light is not strongly absorbed, by reabsorption of the shorter-wave part of the fluorescence emission owing to the band overlap shown in Fig. 43. This effect, which changes the tint of the fluorescence, will vary according to the direction in which the liquid is viewed.

Not only is *external* quenching (as Fig. 41) inhibited by high viscosities, but a similar effect is often noticed for *internal* quenching (as Fig. 42). Certain dyes, non-fluorescent at ordinary temperature in liquid solutions, become fluorescent in 'glasses' of sugar or of boric acid. Similarly, anthracene has a higher fluorescence efficiency in viscous paraffin than in hexane solution. This must be due to the hindering of molecular vibrations in the viscous media so that internal energy conversions of the excited molecule cannot occur.

In solutions of fluorescent substances which are weak acids or bases alterations of pH may cause changes in the fluorescence through change of molecular species (molecule \longleftrightarrow ion). Sometimes both ion and molecule are fluorescent with different colours, and sometimes one species only is fluorescent. Such substances may be used as 'fluorescent indicators', for the titration by strong acids or bases of turbid or coloured liquids (e.g. wine), using the 3,650 Å mercury line for illumination. Examples are quinine (bright blue fluorescence \rightarrow violet at pH 6; violet \rightarrow colourless at 10), 3,6-dihydroxyphthalimide (blue \rightarrow green at 2; green \rightarrow greenish yellow at 7), β -naphthylamine (colourless \rightarrow violet at 3.5), and β -methylumbelliferone (colourless \rightarrow blue at 7).

Fluorescence emitted by crystals is highly polarized, owing to the orientation of the absorbing centres of the molecule to the electric vector of the light. Some polarization may

also be shown by viscous solutions, or by those whose fluorescence is short-lived and feeble through quenching. If the absorbing molecule is so oriented that its chromophoric group is parallel to the electric vector of the exciting light, the emitted fluorescence will have the same vector direction, and its intensity will vary in space according to the curves of Fig. 5. Molecules whose chromophoric groups lie at angles to the electric vector are also capable of absorb-

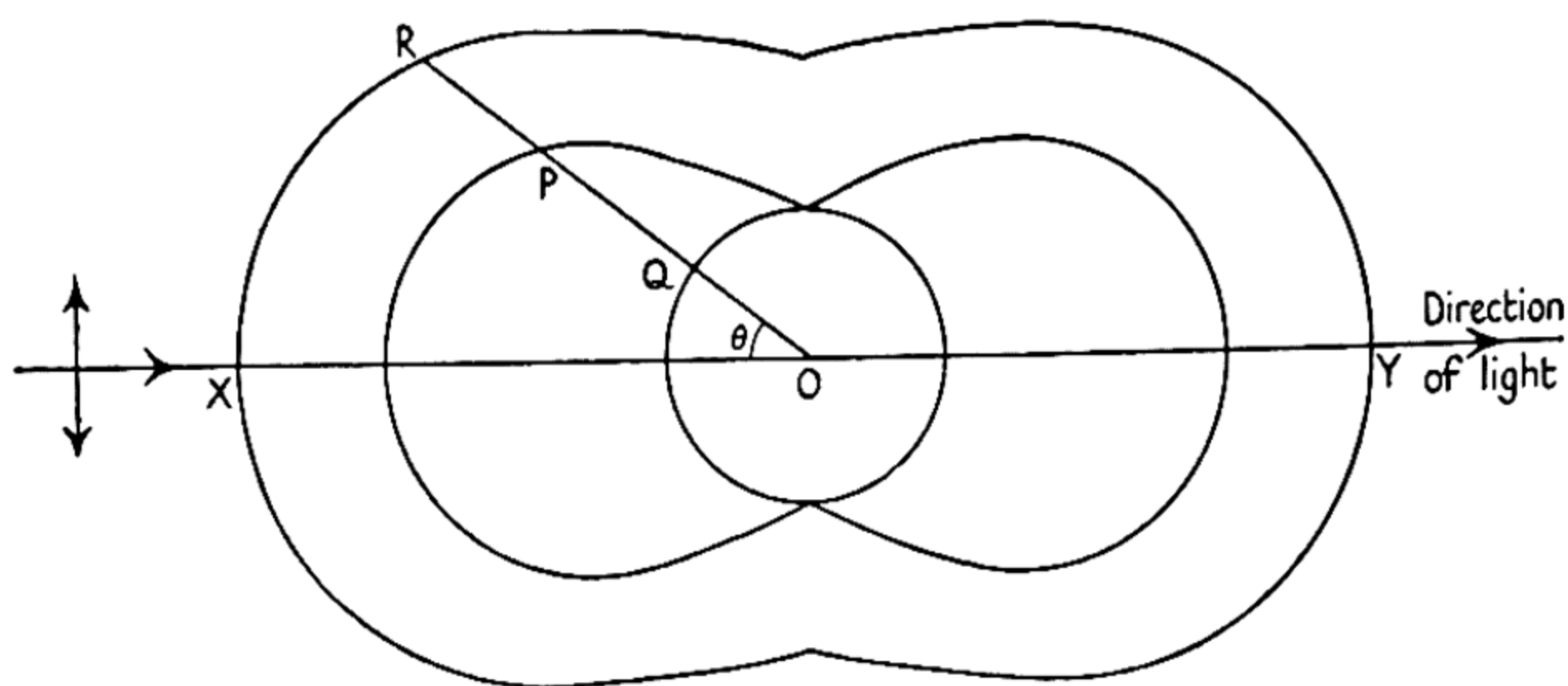


FIG. 44

ing, though with efficiencies diminishing to zero at the angle of 90° , since longitudinal vibrations do not occur in light-waves. The fluorescence emitted from these molecules has its electric vector determined by the chromophoric group direction, and not by the vector of the absorbed light.

If the molecule remains stationary between absorption and emission, it can be shown that for fluorescence excited by plane-polarized light a maximum degree of polarization of 0.5 is observable at right angles both to the light beam and its electric vector. The polar curve of Fig. 44 illustrates the phenomena observed. A ray of light of direction XY , polarized with the electric vector in the plane of the paper, is supposed to be absorbed by an assemblage of fluorescent molecules at O . The lengths of the radii OQ , OP , and OR represent the intensities of fluorescent light making an angle θ with XY polarized with the electric vector at right angles

to the paper, in the plane of the paper, and the *total* light respectively (both polarization directions being at right angles to $OQPR$). For the three-dimensional light distributions the curves must be imagined to be rotated about an axis through O in the plane of the paper and at right angles to XY (cf. Fig. 5).

If now the molecule *rotates* in the period between absorption and emission, the degree of polarization is reduced. Perrin and Lewschin deduced the equation (employing the theory of Brownian movement of rotation)

$$\frac{1}{p} = \frac{1}{p_0} + \left(\frac{1}{p_0} - \frac{1}{3} \right) \frac{RT\tau}{V\eta},$$

where p is the degree of polarization observed at right angles to the beam of plane-polarized exciting light, η the viscosity of the solvent, τ the 'mean life' of the fluorescent molecule, and V its molar volume. p_0 is the limiting value of the polarization in the absence of molecular rotation, and equals $\frac{1}{2}$ if the 'oscillator' forming the absorbing centre of the molecule is linear (i.e. a fixed chemical bond) or $\frac{1}{3}$ if it is circular (linear oscillator rapidly rotating within the molecule).

By varying the viscosity of the solvent (water-alcohol-glycerine mixtures) it is found that for dyes p is nearly $\frac{1}{2}$, and values of τ in good agreement with those determined directly are obtained.

Such direct measurements of the average time between absorption and emission are made by the use of Kerr cells. The Kerr *electro-optical* effect is due to the orientation of molecules in strong electrical fields so that the substance becomes doubly-refracting. It depends both on the normal dipole a molecule may have and on dipoles induced by the field through the polarizability of the molecules. The effect can be used to measure both polarizabilities and dipole moments. It can also be used to construct a 'light shutter' capable of operating to 10^{-9} sec. Such a device is a glass cell

containing purified nitrobenzene and two electrodes to which strong electric fields can be applied. Under the influence of the field the polar molecules orient themselves and the cell behaves as a uniaxial crystal. The light used to excite fluorescence is plane polarized and passed through a Kerr cell and a Nicol prism. The fluorescence light then again passes another Kerr cell between crossed Nicols. When rapidly alternating electric fields are applied to the Kerr cells, the fluorescent light is elliptically polarized, and from its degree of ellipticity the mean life of the excited molecules may be calculated. For highly fluorescent solutions times of about 10^{-8} seconds are obtained; when quenching is present the times are shorter, since the molecules of longer individual period are quenched preferentially. Mean lives may also be estimated from the quenching constants of efficient quenching substances, and in other ways.

The efficiency of the fluorescent process (ratio quanta emitted: quanta absorbed) is a quantity difficult to measure. The best method is to use a spectro-photometer to compare the fluorescence emitted normally from a cell of solution illuminated by white light from a lamp of known energy distribution with a diffusing screen of MgO illuminated with the same light. The total light absorbed is found by graphical integration from the absorption spectrum of the substance and the spectral distribution of the exciting light. The total fluorescent light is obtained by integration of the intensity comparisons of screen and cell at different wave-lengths. For a 'perfect' diffuser and 100 per cent. efficient fluorescer the curves of Fig. 45 apply. The incident light here reaches the diffusing surface AOB at 45° , and the large circle represents the polar curve of scattered light (cf. Fig. 6). Along the normal to the surface the intensity is OX . Now let a fluorescent solution be imagined to be at O . The theoretical light distributions for complete light absorption are shown by the smaller curves; the circle S for freely rotating molecules and

the approximate ellipse F for non-rotating molecules. The latter has not so long an axis as the outer curve of Fig. 44 since the incident light is unpolarized. Along the direction OX the fluorescent intensities are equal, irrespective of the small polarization effects of rotation, and $OY = \frac{1}{4}OX$. When

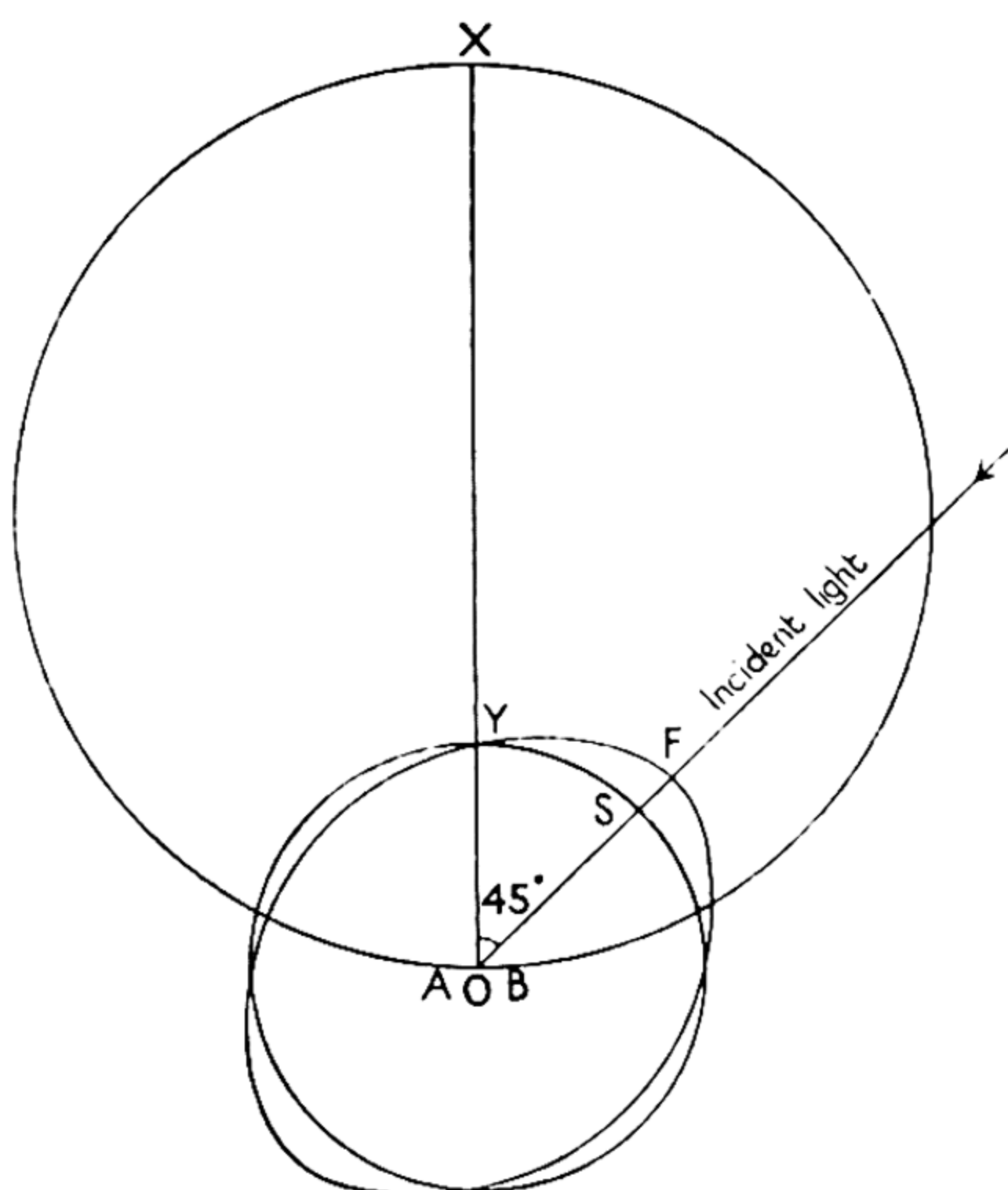


FIG. 45

the efficiency is less than unity OY is smaller. The well-known fluorescent dye-stuffs in dilute solution are found to have quite high efficiencies, that of the sodium salt of fluorescein (uranin) practically equalling unity. It is necessary to use solutions dilute enough to ensure that the light absorption is small to avoid error caused by reabsorption of the short-wave part of the fluorescent light before it emerges from the liquid, as the fluorescent band is overlapped by the absorption band. The observed fluorescence is therefore somewhat feeble and the experiments cannot be made with high accuracy.

The determination of *concentrations* by measurements of fluorescence is not entirely a simple matter. The method is superior to those based on light absorption only at low concentrations where the latter is very small. Care must be taken to avoid the influences of substances which 'quench' fluorescence (e.g. oxygen in some instances), of coloured substances which act as 'inner filters' and absorb the incident light, and of variations in the nature of the solvent, and in the hydrogen ion concentration. It is necessary to use very dilute solutions to eliminate self-quenching, which often occurs in solutions stronger than about 1 gm. per litre, to avoid re-absorption of the fluorescent light with consequent change of tint, and to minimize the effects of the possible presence of other non-fluorescent coloured substances. Values of ϵcd less than 0.01, where ϵ is the molar extinction coefficient for the exciting light, c the molar concentration, and d the cell thickness, must be used if the fluorescence is to be taken as linearly proportional to the concentration to within 1 per cent. Even within this range linearity of scale may depend on geometrical factors of the arrangement of the apparatus, since, if variable apertures are used, different fractions of the fluorescent light may be collected by the instrument at different settings. The best arrangement is to have two horizontal light beams travelling in opposite directions from a lamp (H.P. mercury arc), made parallel by condenser lenses and monochromatic by filters. The beams pass variable apertures and then enter the side (or are reflected up through the bottom) of two rectangular cells, one containing a standard solution and one the unknown. Close to the side of each cell is a photocell to receive the fluorescent light emitted at right angles to the beam; care must be taken that the photocells do not also collect unwanted reflected or scattered light from the beam. A suitable filter cutting off the exciting light and transmitting the fluorescent light is best interposed between the rectangular cells and the photocells.

Rectifier cells serve for strong fluorescences, but vacuum type photocells with electrometer valve amplification are necessary for feeble fluorescence. The outputs from the photocells are connected back to back through a galvanometer, which is used as a null instrument, readings being taken on one of the variable apertures, which should close in such a way as to vary only the illuminated *thickness* parallel to the photocells. Alternatively, variable resistances or potentiometric devices may be used for bringing the galvanometer to zero. A less elaborate apparatus which is often satisfactory and can be used down to high dilutions is a metal tube to hold $\frac{1}{2}$ or $\frac{3}{4}$ inch diameter test-tubes near the bottom of which two inch long rectangular apertures are cut out up the tube normal to two radii at right angles to each other. As near as possible to one aperture is placed a very sensitive valve-amplified photocell or photoelectric electron multiplier, with a filter transmitting fluorescence light but cutting off exciting light interposed. Facing the other aperture, with a filter appropriate for the exciting light, and with or without a condensing lens, is placed a 125 watt H.P. mercury arc lamp. The rectangular apertures should be as wide as possible consistent with their preventing the exciting light directly reaching the photocell. Test-tubes of standards and unknowns can be rapidly inserted, and readings taken of the galvanometer deflexion. This method will measure the fluorescence of a solution of uranin at least as dilute as 1 in 10^6 . For visible estimation of fluorescences an ordinary colorimeter may be adapted, if arranged in such a way that alteration in cup height alters the length of solution illuminated (the light entering horizontally from the front, not from below as for absorption work), or a Pulfrich photometer with suitable filters may be used. With the latter instrument it is very undesirable to have the exciting light exactly in line with the optic axis, since the second filter through which the light passes, and which is intended to transmit the fluorescence while eliminat-

ing exciting light, is never opaque enough to fulfil the latter purpose, if the exciting light is viewed directly through it. Large zero errors due to the same cause may be encountered if an 'in-line' photocell arrangement is used for fluorescence measurement.

For most fluorescence work, qualitative or quantitative, the best illumination is the 3,650 Å line from the mercury lamp. It lies just outside the visible spectrum, and can only be seen as a fluorescence of the eyeball. It is transmitted by glass, and is not short enough in wave-length to harm the eye except when viewed at intensities where visible light of equal wattage would dazzle. This line is easily separated from the other mercury lines by a special 'black glass' containing about 9 per cent. of nickel oxide, and 80 or 125 watt H.P. mercury lamps are obtainable with an envelope of this glass. For the estimation of certain yellow dyes, such as mepacrine, whose absorption band lies at longer wave-lengths, the mercury line 4,360 Å is preferable, and can be isolated with gelatine or glass filters. Where fluorescence is excited only by shorter ultra-violet light, quartz vessels must be used, and the 2,537 Å mercury line, or the 3,000 Å group of lines isolated by suitable filters (see Appendixes).

V

THE LUMINESCENCE OF SOLIDS

MANY solids are caused to emit light by a variety of treatments, among which are illumination by visible or ultra-violet light, cathode rays, X-rays, and α -particles from radioactive substances or protons moving at high velocities. Other less important effects of a secondary character are *crystalloluminescence* (emission of light flashes during crystallization, e.g. strontium bromate), *triboluminescence* (light emission when crystals are crushed, e.g. cane sugar or uranyl nitrate), and such effects as the glow observed when 'insulating tape' is stripped from a roll, or quartz pebbles rubbed together. At low temperatures luminescence is even more common, evidently because quenching processes, i.e. conversion of electronic energy into vibrational energy of the crystal lattice, decreases in effectiveness with lowered temperature.

Two types of light emission are distinguished. *Fluorescence* is usually of short duration (e.g. ruby, 10^{-3} ; anthracene, 10^{-7} ; uranyl salts, 10^{-3} ; barium platinocyanide, 4×10^{-5} seconds; all in the crystalline state). Fluorescence of solids is often of longer duration than that of corresponding solutions (e.g. anthracene solutions, $\sim 10^{-8}$ seconds) which may be related to the 'exciton' processes of the former (see below). The characteristics of fluorescence are (a) proportionality to the incident light intensity, and (b) practical independence of 'half-life period' on temperature, though its intensity may vary with temperature owing to quenching processes. *Phosphorescence* is usually of long duration (several hours), and the term is often used to cover any example of 'after-glow' longer than about 1 second. It is better, however, to reserve the name for phenomena with the following characteristics (a) the 'half-life' (time for

intensity to drop to one-half) rapidly diminishes with rise of temperature, indicating that between absorption and emission the system is in a shallow minimum of potential energy, or 'metastable state', from which it can fall back to lower levels only when it receives thermal vibrational energy sufficient to raise it from the 'potential hollow'; and (b) the crystal shows the phenomenon of 'saturation', i.e. beyond a certain intensity its magnitude no longer depends on the degree of excitation. The 'potential hollows' are often irregularities of structure in the crystal (see below). Phosphorescence in the above sense is usually developed only after crystals have been given heat treatments likely to produce such irregularities. An intermediate type without saturation effects may be associated with an unstable molecular form, as with certain dyes embedded in boric acid 'glasses'. If the 'activation energy' necessary to lift the excited state out of the hollow and permit it to fall back to its original state by radiating its energy is small, the distinction between fluorescence and phosphorescence is blurred; the former term may be applied to the system at high temperatures and the latter at low ones. In considering the question of the effect of temperature on luminescence it is important not to confuse changes caused to the *half-life*, controlled by the activation energy of the metastable state, and changes in *intensity*, controlled by the activation energy of some quenching process.

Most fluorescence and phosphorescence spectra consist of broad bands devoid of fine structure and therefore very difficult to associate with recognizable transitions. Exceptions are the fluorescence of organic compounds and of uranyl and rare-earth salts. Two classes of spectral behaviour may be noticed. Crystalline solids usually show a marked sharpening of their spectra at very low temperatures, due to the suppression of thermal vibrations, etc. The luminescence of glasses, on the other hand, often continues to show

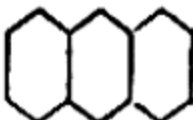
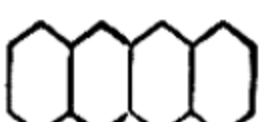
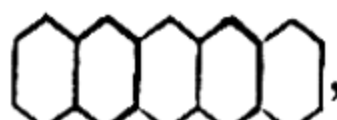
broad bands at low temperatures; here the band width is due to the variable environments of the embedded fluorescent molecules, so that their characteristic frequencies are changed by variable amounts. Such spectra are the most difficult of all to interpret.

Peculiar difficulties arise in attempting to answer the following questions about the mechanism of luminescence:

- (1) Where the light quanta (or cathode rays, etc.) are absorbed, and the nature of the change produced.
- (2) Where the emitted light comes from, and the changes it is due to.
- (3) Whether mobile electrons are liberated or not.
- (4) If the 'centres' of (1) and (2) are not identical, how the energy passes from the absorbing to the emitting particle; whether by movement of 'positive holes' or of 'excitons'.
- (5) The nature of the 'traps' or 'hollows' causing the delayed emission of *phosphorescence*.
- (6) 'Accelerating' or 'quenching' processes affecting the light emission.

Such progress as has been made towards answering these questions is best explained by reference to systems studied in some detail. We must recognize at the outset two classes of luminescent solids. The first class, including uranyl salts, platinocyanides, rare-earths, and anthracene, fluoresce in the highly purified state. In these substances the electron transitions avoid quenching processes by not being strongly coupled to the lattice vibrations; they are either electronic changes occurring in incomplete inner atomic shells or, as in anthracene, the excitation of π electrons which do not play a large part in the valency forces between the atoms (p. 115). The fluorescence of the uranyl salts and the platinocyanides varies with the particular hydrate of the substance; the water of crystallization plays a considerable part in shielding the fluorescent ion from the rest of the lattice. The second class

of luminescent solids, which is much the larger and includes the more important systems, owes its properties to the presence of traces of 'activators' or of special 'impurities' deliberately added to the materials.

A connecting link between the two classes of luminescent solids, 'pure' and 'impurity activated', is found in solid anthracene. Here the strong forces of ionic lattices are absent and the similarity of spectra shows the virtual identity of the processes of fluorescence of both the solid and dissolved state. Highly purified anthracene  fluoresces blue just like its solutions, though more strongly. When the solid contains a minute quantity of naphthacene, , as it normally does unless specially prepared, the green fluorescence of the latter substance appears strongly. Even at naphthacene proportions as low as 10^{-4} the anthracene fluorescence is not visible and the luminescence is almost all from the naphthacene. Similarly a trace of pentacene, , changes the fluorescence to red. Blue light, not absorbed by anthracene, does not excite the green fluorescence unless the naphthacene is present at moderately high concentration and absorbs the light itself directly. In shorter-wave light ($3,650 \text{ \AA}$), where at low naphthacene concentrations all the light is absorbed by anthracene molecules, the green fluorescence of the impurity still appears, suppressing the blue fluorescence of anthracene itself. It can be shown from the magnitudes of the extinction coefficients and from the fact that the green fluorescence is not shown when the impure anthracene is dissolved in benzene that this is not due to the primary emission of anthracene fluorescence followed by reabsorption and re-emission by the impurity. We must therefore assume an 'exciton' or optical resonance process (p. 149). The anthracene molecules in the solid absorb quanta, and these are handed on from molecule to molecule so that the excitation energy wanders through the crystal. The naphthacene absorption

band overlaps that of anthracene on the long-wave side, so that when the wandering excitation energy reaches a naphthacene molecule it 'falls in', becomes a quantum of longer wave-length (the excess energy being lost to the lattice as heat vibrations) and so is 'trapped' until released again as the fluorescence characteristic of the impurity. Evidently even in the absence of naphthacene an 'exciton' movement occurs in anthracene crystals, so that the absorbing and emitting molecules are not the same. The effect doubtless arises from the interactions of the π electrons of these molecules, and leads to depolarization of the emitted fluorescent light.

Zinc sulphide is a typical inorganic luminescent substance. In the absence of foreign activators it fluoresces (blue) only when heat-treated to give excess zinc as 'excess cation'. More brilliant effects are obtained with 1 part in 10^4 of copper chloride (green) or silver (blue) as activators. The *fluorescence* is of moderately long duration, and with special heat treatment a *phosphorescence* lasting an hour or so is developed. The fluorescence and phosphorescence spectra are identical, so that the processes differ only in that the latter involves an intermediate metastable state. Zinc sulphide phosphors show photoconductivity on illumination, and the decay curves of the fluorescence and the phosphorescence are usually hyperbolic (or 'bimolecular') and not exponential (or 'unimolecular') in character. These facts indicate that the primary effect of the absorbed light is to liberate mobile electrons within the crystal which return (giving light emission) to a different site from the point of liberation. The luminescence of zinc sulphide caused by cathode rays and other rays or high-speed particles also arises from mobile electrons produced in the crystal. Certain additional facts are important for unravelling the mechanism of light production. The absorption spectrum at longer wave-lengths depends somewhat on the activator present, but at shorter wave-lengths this is not so. The emission spectrum, however,

does not depend on the wave-length of the light absorbed, but varies greatly with the activator. We thus conclude that the light may be absorbed partly by the activator at longer wave-lengths, while at shorter wave-lengths it is absorbed by the ZnS crystal (though not necessarily by the crystal free from all lattice imperfections; in a perfect crystal the absorption in the short-wave ultraviolet is characterized by extinc-

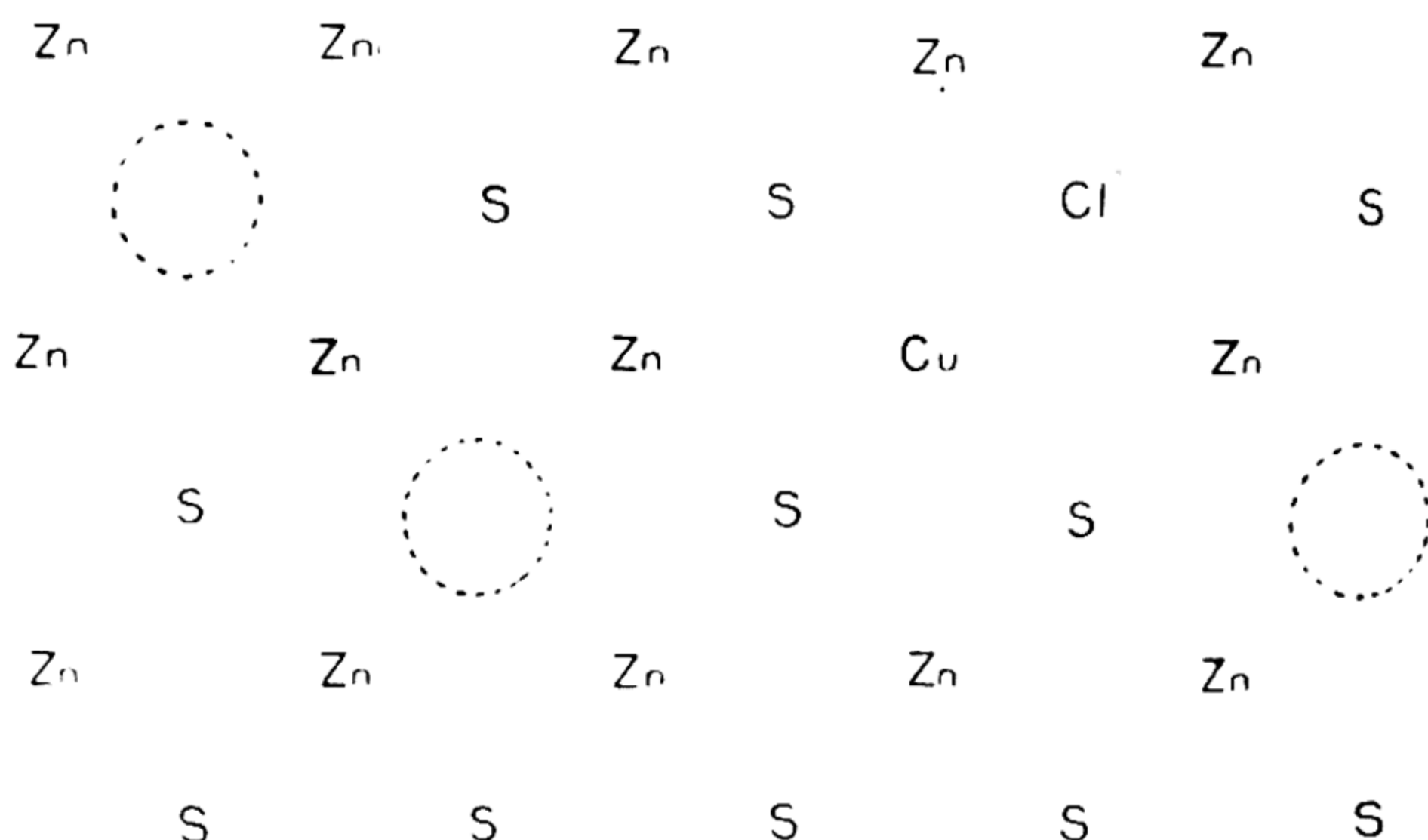


FIG. 46. Dotted circles = F centres, i.e. lattice points where an electron takes the place of an anion

tion coefficients many thousand times greater than those observed for light absorption in the ordinary excitation regions of zinc sulphides). The emitted light must be assumed to come entirely from the activator atoms. These facts must be reconciled with the observation that the efficiency of light emission is almost 10 per cent. when α -particles or light quanta are absorbed, although the activator is present only at proportions of 10^{-4} , and cannot preferentially be affected. There must exist some process whereby energy is transferred from the sites of absorption to the sites of emission. The following mechanism appears the most reasonable way of interpreting the facts:

Fig 46 represents the lattice of ZnS. The crystal forces

between the Zn and S are partly ionic and partly covalent in character. As an approximation we may regard the lattice as composed of Zn^+ and S^- ions, each ion having also covalent links with its neighbours, the partners continually changing. By the heat treatment necessary for luminescence the crystal has lost sulphur atoms to leave an excess of zinc atoms. Copper associated with chlorine is shown as the impurity activator. The dotted circles are F centres, i.e. vacant anion lattice sites occupied by an electron. The luminescent properties must then be considered under several heads.

1. *Zinc sulphide with excess zinc only*

(a) *Light absorption 4,000–3,300 Å.* Light quanta are absorbed probably by zinc atoms which liberate mobile electrons into the lattice. These electrons move on the 'conduction band' of the lattice and confer photoconductivity on it. The Zn^+ remaining may recover an electron from a neighbouring zinc or sulphur ion, so that the 'positive hole' or 'electron defect' wanders about through the lattice. The mobile electron eventually returns to a positive hole, reforming a neutral atom and emitting (blue) fluorescence radiation.

(b) *Light absorption at wave-lengths shorter than 3,300 Å.* Light quanta are here probably absorbed by the S^- ions of the lattice; mobile electrons are liberated into the conduction band, and the positive holes on the anions move to zinc atoms. The emission is then as in (a).

2. *Zinc sulphide with copper activation*

(a) *Light absorption 4,000–3,300 Å.* Zinc atoms and to a lesser extent copper atoms absorb quanta and emit (in the former case) mobile electrons into the lattice. The positive holes move from the zinc and become finally located at the copper, Cu becoming Cu^+ . Owing to the lower energy level the positive hole thereby loses its mobility. The mobile electrons become captured by the positively charged copper ions

which then lose energy and emit the characteristic green fluorescence of the copper activator.

(b) *Light absorption at wave-lengths shorter than 3,300 Å.* As 1 (b) followed by 2 (a) above.

(c) *Effect of α -particles or X-rays.* Mobile electrons and positive holes are formed by secondary processes and behave as in 2 (a).

(d) Some of the mobile electrons may be trapped at certain positions of energy minima within the crystal, from which they are liberated again only when they receive sufficient heat energy to lift them out of the 'potential hollow' or 'energy trap'. The long and very temperature-sensitive delay, so caused before they can return to activator centres represents the phenomenon of phosphorescence. The nature of the traps is uncertain. They may be internal cracks, or F centres, i.e. sites vacated by a sulphur ion and occupied by an electron. Such centres are known to exist in sodium chloride crystals which contain excess sodium atoms, where they can take up a second electron (to give an F' centre), and the second electron is easily released again by moderate thermal energy. Their existence in zinc sulphide is postulated merely by analogy, not by experimental proof.

3. *Zinc sulphide with manganese as activator*

(a) At long wave-lengths the Mn^{++} ions absorb quanta and pass into excited states *without* liberating mobile electrons. Fluorescence characteristic of the activator and *no phosphorescence* is observed.

(b) At short wave-lengths process 1 (b) occurs, i.e. mobile electrons are emitted by the lattice, and both positive hole and then mobile electron reach the Mn^{++} ion. Both fluorescence and phosphorescence occur, and the time-decay curve is hyperbolic and not exponential as in 3 (a).

The progressive substitution of cadmium for zinc in the copper activated sulphide phosphors causes the luminescence

to change from green to red; the same change is produced in manganese activated silicate preparations described below when beryllium is substituted for zinc. These red phosphors are of importance in fluorescent lamps and for cathode-ray screens.

The sulphides of the alkaline earths have long been celebrated as phosphors. When activated by 1 part in 5×10^3 of bismuth (for example) they show phosphorescence of many hours' duration, but the intensity of their emission and their sensitivity to cathode rays, etc., is less than that of zinc sulphide. The processes occurring are more complicated than those of ZnS, and are rendered still more difficult to interpret because of the unknown condition of the material, which needs fluxes to secure the entry of the activator into the sulphides. The fluorescence and the phosphorescence are excited by somewhat different spectral ranges and they have different emission bands; further, several luminescent processes are simultaneously possible (partly separable by the use of different temperature ranges) of different emissions and of different lifetimes. The absorption bands of the material, which vary with different activators, fade during illumination and are replaced by others. The nearest approach to an interpretation is that the light is absorbed by a bismuth-sulphur complex which undergoes a photochemical change of a reversible type. Mobile electrons are liberated into the lattice, and ultimately recombine with other activator centres, producing luminescence. Phosphorescence is due to the existence of electron traps, and the saturation effect may be due to the temporary exhaustion of the primary absorbing centres.

Infra-red light exerts one of two effects on these substances, dependent on the wave-length. If a phosphor which has been excited is exposed to long-wave radiations the trapped electrons are either released with a rush, so that a brilliant though brief emission of the stored light occurs, or thermal quenching

is promoted, so that the phosphorescent glow is reduced in intensity and in total emission.

Another important type of luminescent substance is zinc orthosilicate activated by manganese. The excitation needs ultra-violet light shorter than $2,600 \text{ \AA}$ or high-speed particles. The emission is a structureless band in the green, and the decay is exponential. This may either mean that excited states only and no mobile electrons are liberated or may be because the number of 'traps' in the crystal is much less than the number of 'luminescence centres'. In this case it can be shown mathematically that temperature-insensitive exponential decay laws may take the place of the usual hyperbolic temperature-dependent decay associated with the liberation of mobile electrons. As the crystal shows photoconductivity, the latter alternative is the more probable. Zinc beryllium silicate behaves similarly, having a pink fluorescence. The activator in the above silicates, manganese, is responsible for producing fluorescence in many other substances, including glass, calcite, etc. The tungstates (sometimes activated with lead) have an exceedingly rapid exponential decay ($\approx 10^{-7}$ sec.). Calcium tungstate fluoresces blue and magnesium tungstate white. Cadmium borate is another luminescent material of technical interest.

The ruby is a peculiarly simple type of fluorescent solid whose spectrum can be completely interpreted. The crystal consists of chromic ions in solid solution in an aluminium oxide lattice. Light is absorbed by the chromic ions to give a transition analogous (though modified by the solid state) to a known electronic transition in the spark spectrum of chromium. No mobile electrons are liberated. The activated chromic ions return to their normal level after about 2×10^{-3} sec. by re-emitting the light as fluorescence. Because of the coupling of the ions by valency forces in the lattice, excitation of the chromium ion may be accompanied by excitation of a lattice vibration, similar to the behaviour

of a diatomic molecule (p. 88). The fluorescence on this account consists of a number of lines separated by frequency intervals corresponding to vibrations of the Al_2O_3 lattice; the lines being quite sharp since the excited electron is deep down in the chromium ion and is only little more affected by its environment than if the ion were in the gaseous state. It can be shown that the above statement does not reduce to two mutually contradictory hypotheses, that the ion is coupled to its neighbours and yet is independent of them. The 'fluorescence' electron is not a valency electron.

The diamond also frequently shows a line fluorescence, generally blue, though the intensity and the colour vary very much with the specimen. Phosphorescence is also shown by certain diamonds. The relationships of these effects to lattice irregularities and to impurities present have not yet been settled.

Luminescent solids have recently assumed great technical importance in a number of ways, particularly for lighting (p. 53) and for luminous screens for television, etc. Mixtures of zinc and cadmium sulphides activated with silver or copper, or zinc beryllium silicates activated with manganese, or magnesium tungstate, give fluorescence varying in colour from red through pale cream, pink, or white, to green and blue. The sulphides are used inside an outer envelope to add red to mercury lamps, while silicates and tungstates are used inside the actual discharge tube of the lamp (mercury or neon) to utilize the short ultra-violet emission. Luminescent intensities as high as $1\frac{1}{2}$ million foot-lamberts are obtainable with 70,000-volt electrons for momentary scanning in a cathode-ray tube. High intensities of phosphorescence are never obtainable since the total amount of light which can be stored is limited by the number of 'traps' or similar requirements of phosphorescence. In good phosphors about 10^{-2} cal. of light energy can be stored per gram, and this corresponds to the excitation of practically all the active centres

of the substance. Zinc sulphide phosphors give a brilliant phosphorescence falling almost to zero after one hour, while strontium sulphide phosphors (Bi act.) appear feebler because the emission lasts longer—several hours. Fluorescence in ultra-violet light of the strong mercury line 3,650 Å is empirically used for the examination of fossils, bones, teeth, minerals, drugs, paper, adsorption columns in 'chromatographic analysis', etc. The nature of the luminescent processes are usually obscure, but they seem more often due to the effects of impurity activators than to the bulk substance.

Impurity molecules in solid solution in crystals often fluoresce more strongly than in their own solid state, owing to lessened deactivating influences. Molecules embedded in glasses, resins, or nematic or smectic phases, as manganese or rare-earth ions in glasses, rhodamine in transparent resins, or fluorescein in boric acid or glucose glass, or in smectic ammonium oleate solutions, are often in a very favourable condition to show fluorescence. The fluorescence of manganese in glasses is interesting because of its dependence on the position of the ion in the glass structure. In the 4-coordinate MnO_4 form, where the manganese replaces silicon in the glass, a green fluorescence is shown, while interstitial Mn^{++} ions fluoresce red or orange as in manganese salts. Light emission of a type intermediate between fluorescence and phosphorescence is often observed in glasses, lasting several seconds and with a half-life moderately dependent on temperature. An example is fluorescein dissolved in boric acid glass. The emission spectrum here is composite, different band systems appearing at high and at low temperatures. Metastable excited states of the molecule must be assumed, capable either of slow return with one type of emission to the ground state or of thermal excitation to a higher state which returns to the ground state emitting different bands and having a temperature-sensitive half-life. In some instances the delayed emission seems associated with the presence of a dye

molecule in a dimeric form, as with dye-stuffs adsorbed on silica gel. Here the delay would arise from the to and fro passage of the energy between the molecules; the usual competing quenching mechanisms which operate on polymerized dyes in solution for some reason not being operative. The fluorescent and phosphorescent mechanisms of minerals such as fluor-spar, aragonites, etc., are generally unknown; in some instances they arise from impregnation with organic compounds such as porphyrins or waxes formed by decomposition (e.g. in fossils), but are more often likely to be due to the presence of unknown inorganic 'activators', in some instances rare-earth ions.

In the preparation of phosphors the greatest care must be taken to avoid unwanted impurities, which can exert powerful effects in reducing both the intensity and the duration of the emission. They evidently introduce new electron-removing centres into the crystal, at which recombination of electron and positive hole occurs without the emission of light.

VI

PHOTOCHEMICAL REACTIONS

THE aim of the investigation of photochemical reactions is to discover the mechanism of the chemical changes which take place when a system is exposed to light. Generally, these reactions are complex in nature, and the actual measured change is rarely that directly produced by the light. It is necessary, therefore, to distinguish between the 'primary' effect of the light and the 'secondary' thermal reactions which follow. In gaseous systems the nature of the spectrum, whether fine-structured, diffuse, or continuous, or whether fluorescence is emitted, will, subject to the considerations discussed in Chapter III, enable a decision to be made as to whether the molecule dissociates or not. This information is not so readily obtained for reactions occurring in liquids.

Photochemical reactions usually differ from thermal ones in that the energy of activation is wastefully employed. For example, the thermal decomposition of HI takes place by the mechanism $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$, the colliding HI molecules needing a joint energy of 44 kilo-calories to react. The energy needed for thermal activation is rarely large enough to raise the molecules to electronically excited levels; photochemical activation always proceeds through such a mechanism. In the photochemical reaction at least 67.7 kilo-calories are required for each HI molecule, which reacts by the primary change $\text{HI} + h\nu \rightarrow \text{H} + \text{I}$. This illustrates a very common feature of photochemical reactions, the formation of free atoms or radicals, whose subsequent reactions give rise to the complexity of the measured chemical changes. The subsequent reactions in the above example are relatively simple, namely, $\text{H} + \text{HI} \rightarrow \text{H}_2 + \text{I}$ and $\text{I} + \text{I}(+\text{M}) \rightarrow \text{I}_2(+\text{M})$.

The following of a photochemical change is a very difficult

matter. In the first place, the complexity of the secondary reactions often makes the mere observation of a pressure change, or estimation of one product by titration, insufficient for the purpose, and an elaborate analytical procedure at various stages of the reaction is usually necessary. This is made peculiarly difficult by the second consideration, that the amounts of chemical change are small. Ordinary monochromatic light sources do not commonly send more than $10^{-4}Nh\nu$ per hour to a cell under the experimental conditions. If the number of molecules reacting is comparable with the number of gram-molecular quanta, a hundredth normal solution only changes in concentration by a few per cent. in this time.

The absorption of monochromatic plane-polarized light in an isotropic medium is given accurately by Lambert's law, $-\frac{dI}{dx} \propto I$, where x is the distance traversed by the light through a substance, and approximately by Beer's law, $-\frac{dI}{dc} \propto I$, where c is the concentration of absorbing material (or pressure of an absorbing gas). Deviations from the latter law occur when the absorption spectrum of the substance is affected by concentration, as by disturbance of electronic levels through collisions or by the grosser cause of polymerization (e.g. NO_2 gas, or certain dye solutions). In non-cubic crystals the absorption varies with the direction of the electric vector of the light; in liquids or solutions this effect only occurs where the molecules are partly oriented, e.g. if filamentous colloid particles are lined up by streaming of the liquid. In the integrated form the above laws may be combined to give the expression:

$$\frac{\text{light transmitted through thickness } d}{\text{light incident}} = e^{-\epsilon'cd} \text{ or } 10^{-\epsilon cd}.$$

$$(\epsilon' = 2.303\epsilon).$$

The fraction of light absorbed is therefore $(1 - 10^{-\epsilon cd})$, which approximates to $\epsilon'cd$ when the absorption is feeble. ϵ is called the molar extinction coefficient (c in gram molecules per litre).

The quantity ϵcd $\left(= \log_{10} \frac{\text{light incident}}{\text{light transmitted}} \right)$ is called the 'optical density'. If several absorbing layers are successively traversed by monochromatic light the overall 'density' is the sum of the separate 'densities' of the layers. The table below gives values for the light absorption and transmission for different values of ϵcd .

TABLE 6

ϵcd	<i>Fraction of incident light</i>	
	<i>Absorbed</i>	<i>Transmitted</i>
Very small	$2.3 \epsilon cd$	1
0.05	0.11	0.89
0.1	0.206	0.784
0.2	0.367	0.633
0.3	0.500	0.500
0.4	0.602	0.398
0.5	0.684	0.316
0.6	0.749	0.251
0.7	0.800	0.200
0.8	0.842	0.158
0.9	0.874	0.126
1.0	0.900	0.100
1.3	0.950	0.050
1.7	0.980	0.020
2.0	0.990	0.010
3.0	0.999	0.001

Most accurate range of *transmission* for estimation of concentration = 20–56%

In applying these figures it must not be forgotten that ϵ is constant only for monochromatic radiation and may also vary with the direction of polarization of the light; the fraction of light absorbed by a layer of substance when polychromatic light or non-cubic crystals are concerned can only be evaluated by splitting up the calculation into parts.

When values of ϵ or of $\log_{10} \epsilon$ are plotted against wave-

length or frequency for any substance or solution, the graph is called a 'light-absorption curve'.

To calculate the order of magnitude of photochemical changes the following assumptions may be taken for purposes of illustration. We imagine a photochemical cell of volume 20 c.c. and depth 1 cm. Let the photoactive substance have a molecular weight of 200 and a density of 1. If the cell is filled with the pure substance, we have $c = 5$, $d = 1$, and contents of cell = 10^{-1} gm. molecules. Taking the incident light as about 10^{-7} gm. molecular quanta per sec., we find that to activate one-tenth of the material (10^{-2} gm. molecules) an exposure of 30 hours will be required, assuming strong absorption, i.e. $\epsilon cd > 1$, or $\epsilon > 0.2$.

Assuming now the cell to contain a solution of concentration $M/10$, the time for one-tenth of the molecules to receive a quantum is about 40 minutes with strong absorption, $\epsilon cd > 1$, or $\epsilon > 10$.

For the case of weak light absorption we have (light absorbed) = $2.3\epsilon c$, and we find that to activate one-tenth of the cell contents the exposure must be $2.4/\epsilon$ hours, independent of c , provided c is less than 0.1.

As another illustration we may assume the substance spread as a single monolayer of thickness 5.5×10^{-8} cm. The time for one-tenth activation, assuming a surface 5×5 cm., containing 10^{16} molecules, is exposed to incident radiation of 10^{17} quanta per sec., is

$$10^{-2}/2.3\epsilon cd = 1.6 \times 10^4/\epsilon \text{ seconds.}$$

The actual amount of chemical change produced in the above systems depends on the relation between molecules 'physically activated' by absorbing a light quantum and final chemical changes ensuing. The ratio (number of molecules chemically changed)/(number of quanta absorbed) is called the 'quantum efficiency', and its importance was first emphasized by Einstein. It is rarely exactly unity; it is commonly of that order of magnitude, but may vary from

exceedingly low values, as with light-stable dyes, to a million or so, as in sensitive H_2 Cl_2 mixtures where light initiates 'chain reactions'. Where photochanges are complex, as in the photolysis of most organic compounds, we may define quantum efficiencies in more than one way, by reference to the number of molecules of reactant decomposed, or to the number of molecules of any product formed in the change. Quantum efficiencies usually vary with changes of conditions (wave-length, concentrations, etc.) and in certain reactions are not independent of the light intensity.

The arrangement of a photochemical experiment is usually as follows. A powerful and constant light source is provided with a short focus condensing lens to give an intense beam. This is rendered monochromatic (or nearly so) either by the use of a specially designed monochromator or by filters (see Appendix II). For the visible region a Christiansen filter may be used. This is a cell containing granules of glass in methyl benzoate which is placed in a controllable thermostat. The two materials have very different dispersions, and at a fixed temperature the refractive indices coincide at one wave-length only. Light at or near this wave-length is then freely transmitted, while other wave-lengths are scattered away in all directions. With a suitable arrangement of lenses and stops, narrow bands from any part of the visible region may be isolated. The light beam then falls on a parallel-walled cell, usually of fused silica, or the plastic 'Perspex', 2–6 cm. in diameter and 0.5–5 cm. from front to back. Stirring, mechanical or electromagnetic, is often required for solutions. The chemical change is followed by methods adapted to the nature of the reaction; pressure changes, with or without condensation of volatile fractions, chemical analysis, and changes in the light absorption. When the light is feebly absorbed the rate of the *primary* reaction is proportional to the product of the extinction coefficient and the concentration ('unimolecular' rate law), while for total

absorption the rate is constant ('zero order' law) with time. The presence of other (inert) light-absorbing substances in the system ('inner filters') introduces complications. If ϵ_1 and c_1 are the extinction coefficient and concentration of the photo-active substance and ϵ_2 and c_2 those of the inner filter, the fraction of the light absorbed by the former is

$$\frac{\epsilon_1 c_1}{\epsilon_1 c_1 + \epsilon_2 c_2}.$$

Two quantities relating to the light beams have to be measured: the total light falling on the cell and the fraction absorbed by the system. The former may be done in two ways: by the use of a thermopile (Appendix III) or by actinometry. For details of these methods references must be consulted. The fraction of light absorbed may also be found by thermopile measurements, but if it is small it is better determined with a photocell or by the methods of absorption spectroscopy. The 'quantum efficiency' is then calculated from experiments made over as wide a range of light intensity, wave-length range, temperature, and concentrations of reactants (and other substances which may affect the reaction) as possible. These results constitute the 'kinetics' of the change, i.e. the laws of dependence of the photochemical rate with the above variables. The next step is to attempt to elucidate the reaction mechanism. Except in simple cases this can rarely be done without ambiguity.

Since the mercury lamp is commonly used for photochemical work the approximate data on light emission given in Table VII below are useful.

Intensities about ten times these values are obtainable at the exit slit of a *f.* 3.5 monochromator with a capillary lamp taking a similar current, but the utilizable area is less.

Low-pressure mercury lamps containing about 5 mm. of He or Ne designed to give chiefly the 2,537 Å line emit sideways about $3 \times 10^{-7} Nh\nu$ per sec. per cm. length of lamp tube.

TABLE VII

<i>Mercury line, Å</i>	<i>Nhν/sq. cm./sec. at 10 cm. from a lamp taking 3.5 amp. at 130 volts</i>
Yellow { 5,790 5,770	30×10^{-9}
Green 5,461	22×10^{-9}
Blue 4,358	16×10^{-9}
Violet 4,046	7×10^{-9}
3,650	22×10^{-9}
3,130	13×10^{-9}
Ultra- { 3,020 Violet { 2,804	6×10^{-9}
2,654	2×10^{-9}
2,537	3×10^{-9}
2,537	2×10^{-9}

The light output of a mercury lamp depends on three variables, arc current, arc voltage, and pressure of mercury vapour; the latter depending on the temperature of the arc tube (usually 300–400° C.). Of these variables only two are independent; consequently control of the heat loss of the lamp is as important in maintaining constant output as control of the current or voltage.

In attempting to find plausible mechanisms for photochemical reactions, especially those of simple molecules in the gaseous state, it is often necessary to have recourse to reaction velocity theory to decide which possibilities to include or exclude. The procedure is to write down all conceivable secondary reactions which the atoms or radicals or excited molecules formed in the primary process might undergo, not forgetting possible chain or wall reactions. Some of these can be eliminated because they will not satisfy the measured kinetics on applying the condition that the rate of change of unstable intermediate concentrations must be zero (see the $\text{H}_2 + \text{Br}_2$ reaction below). Others are eliminated because they are of the bimolecular form $A + B \rightarrow C$ (two molecules giving *one* molecule), which is not possible if *A* and *B* are small molecules, since it is unlikely that the

energies of A and B will exactly equal one of the quantized levels of C (another molecule M must be introduced on both sides of the equation to carry off excess energy in the kinetic form). Highly endothermic reactions may be regarded as improbable. The question is then: Which of the remaining reactions actually represent the mechanism? It may be possible experimentally to introduce atoms or radicals by other means into the system to see if they react at measurable rates. Sometimes a purely theoretical treatment is all that is possible. The rate-constant k of a bimolecular reaction, expressed as $\text{moles}^{-1} \text{sec.}^{-1} \text{c.c.}$,

$$= 10^{13} e^{\Delta S/R} \cdot e^{-\Delta H/RT} \approx 10^{14} e^{-E/RT},$$

where ΔS is the entropy change and ΔH the heat content change in the 'activation' of the system, and E is the 'heat of activation' as deduced from the temperature coefficient. Any reaction with a heat of activation less than about 16 kilo-calories per mole is then almost certain to be fast at the ordinary temperature. Incidentally this shows that photochemical reactions cannot extend beyond about 18,000 Å since the thermal supply of quanta of long wave-lengths would exceed the supply from radiation, i.e. the reaction would proceed rapidly in the dark. A limit thus exists to the possibility of sensitizing photographic plates to the infra-red. In elementary reactions, where the energy of activation is unknown, it may sometimes be obtainable by the 'transition state' theory of reaction velocity. The energy of activation of a reaction such as $AB + C \rightarrow A + BC$ can in principle be calculated by formulae developed by London for the relations between the energies of the diatomic molecules and the triatomic complex ABC . The former are given by the potential energy-distance curves of the molecules AB and BC . The approach of the atom C to the molecule AB along the $B-A$ line is considered; this will give the lowest energy necessary for reaction, since the atom A then exerts the least repulsive force on C . A three-dimensional potential-energy diagram

the bromine atom is imagined to be brought up to the H_2 molecule, the system follows the curve of lowest possible potential energy, i.e. from P it goes up the valley past the 5, 10, 15, and 20 contours till it reaches an 'energy pass' at Q , representing the transitional state $\text{H} \dots \text{H} \dots \text{Br}$, whence it can pass downhill towards R , i.e. towards an HBr molecule with an H atom at infinite distance. As the bulk of the reacting molecules take the easiest path from P to R , i.e. over the pass Q , the height of Q represents the energy of activation. This representation is extremely valuable in visualizing the meaning of heat of activation; unfortunately as a means of quantitative calculation it is subject to great possibilities of error through the difficulties of evaluation of the potential energy surfaces from the data of the diatomic molecules. The treatment of this problem is as follows. A molecule exists in a large number of quantized energy states, of electronic, vibrational, rotational, or translational character. The latter states can be considered as 'non-quantized' when large volumes of material are considered. Every energy state has a certain 'probability', which can be expressed by the equation

$$\frac{N_1}{N} = \frac{e^{-E_1/RT}}{\sum e^{-E/RT}},$$

where N_1/N is the fraction of molecules in an energy state E_1 and $\sum e^{-E/RT}$ is the sum of the exponential functions over *all* the possible states. This latter quantity is called the 'partition function', and its value for translational and *simple* vibrational or rotational states can be expressed in terms of the molecular frequencies and moments of inertia obtainable from spectroscopic data. The theory of partition functions is dealt with by Statistical Mechanics, an enlarged and 'molecular' form of Thermodynamics. The 'partition function' f is related to the free energy F by the relation $F = -RT \log f$, and therefore chemical equilibrium constants, which are related to F by the van 't Hoff isochore, can be written as

products of partition functions. Now in a reaction such as $AB + C \rightleftharpoons ABC \rightleftharpoons AC + B$ the theory of partition functions can calculate (in principle) the equilibrium constant $\frac{(ABC)}{(AB)(C)}$

where ABC is the 'transition complex' representing the state of the system at Q . The vibrational energies of the transition complex are given by the shape of the potential energy surface near Q ; the complex differing from an ordinary molecule only in that one of its vibrations (over the 'pass' at Q) leads to dissociation. The reaction velocity is equal to

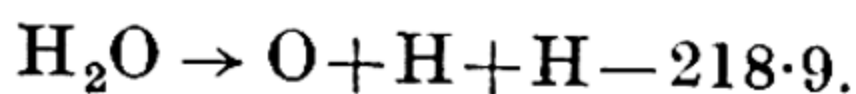
$\kappa \frac{kT}{h} \times \frac{f_{(\text{complex})}}{f_{AB} \times f_C} e^{-Q/RT}$, where κ is the fraction of complexes

which pass over the barrier at Q , $\frac{kT}{h}$ comes from the partition

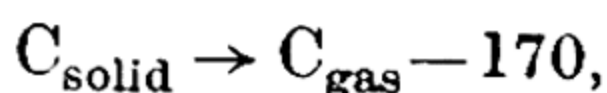
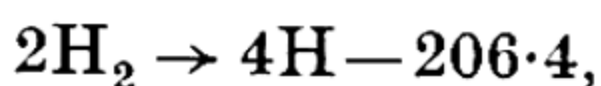
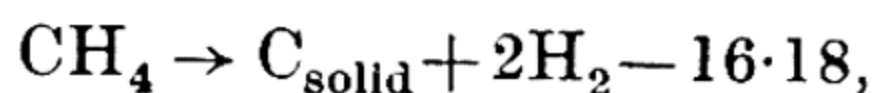
function of translation for the complex along the dissociation path, and the remainder of the expression gives the 'equilibrium constant' of the complexes. κ is usually taken as $\frac{1}{2}$, but may be very much less for certain curvatures of the potential energy surfaces near Q . With so many quantities very inadequately known the final result for the absolute reaction rate cannot be expected to be very accurate, but where relative rates of two reactions are concerned it may be used with more confidence.

In attempts to discover the most probable photochemical mechanism of a reaction it is important to know whether the quantum of energy of the light employed is large enough to break any particular link in a molecule. For diatomic molecules, 'bond energies', or energies of dissociation into atoms, may often be found by a study of their spectra (convergence of vibrational levels; if these refer to an upper state of the molecule, correction must be made for the fact that the atoms produced may not be in their ground-level). The following dissociation energies, for example, are obtained in this way: O_2 117.2, N_2 170, Na_2 17.6, C_2 83, Cl_2 56.9, Br_2 45.2, I_2 35.4 kilo-calories per gram molecule. The dissocia-

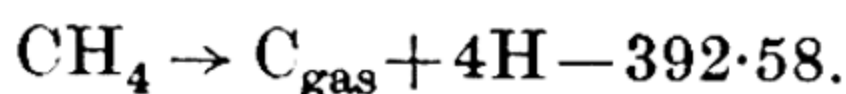
tion energy of H_2 , 103.2, can be calculated by wave-mechanics or measured experimentally, and those of molecules such as HCl (102), HBr (86.3), and HI (67.7) are found by combining the known energies of dissociation of hydrogen and the halogens with the thermochemical heats of formation. Difficulties arise in attempts to extend the concept of bond energy to polyatomic molecules. In the case of the water molecule, by combining thermochemical data with the energies of dissociation of hydrogen and oxygen we have



Spectral evidence shows that the energy necessary to split one hydrogen atom off the water molecule is about 119.5, and to dissociate the OH radical about 99, while the $\text{O}-\text{H}$ bond energy from water is $\frac{1}{2}(218.9) = 109.5$ kilo-calories per gram molecule. The data are not entirely reliable, but seem to show that bond energies cannot be regarded as constant in different molecules. For methane we have the following equations:



whence



The bond energy $\text{C}-\text{H}$ is thus $\frac{1}{4}(392.58) = 98.1$. The above calculation, however, is subject to the uncertainty of the heat of volatilization of carbon. One way of obtaining this is by optical measurement of the temperature of the positive pole of the carbon arc burning under different inert gas pressures; the experimental values give the vapour-pressure curve of carbon from which the latent heat of evaporation at ordinary temperatures may be calculated by the application of thermodynamics. The measurements themselves are of great difficulty, and are affected by such considerations as the degree to which the carbon vapour can

be taken as monatomic. The carbon atom exists in three 'unexcited' states (p. 105) and the energy change lowest ground state \rightarrow quadrivalent state must be considered. Other methods using spectroscopic data relating to the molecule CO, for example, give more accurate numerical results with some uncertainty, however, as to the level of the C atom concerned. The bond energy as calculated above is probably accurate to ± 4 k. calories.

If now an attempt is made to find the heats of linking in a molecule such as formaldehyde $\begin{smallmatrix} \text{H} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{H} \end{smallmatrix}$, the value for the C=O bond can only be evaluated if the C—H bond energy is taken as equal to that for methane or for the C—H radical. This assumption is not justified, and the result is that bond energies of polyatomic molecules cannot be estimated with accuracy. In certain cases approximations to energies of linking in molecules may be obtained from 'pre-dissociation' limits in the spectra or from spectral limits of fluorescence, the disappearance of which at short wavelengths points to dissociation of the excited molecules. Application of wave-mechanical methods assisted by considerations based on the spectra indicate that bond energies in molecules are almost always affected by 'conjugation'. In benzene the effect is very marked, and it is not negligible in even a 'saturated' molecule as ethane. No chemical bond can be regarded as of a strictly 'unit' character. The bonding electrons are not confined to certain links; their effect extends in varying degree round the molecule. If a molecule is imagined to be formed from its component atoms by the coupling of electrons in pairs to form links, allowance must be made for a redistribution of the 'electron density'. Some bonds 'donate' and others 'accept' electron density. In benzene the 'double bonds' formed in the above imaginary and incomplete picture of molecule building donate some of their character to the single bonds; the system as a whole

gains in stability and the effect on the acceptor bonds is greater than that on the donors. This is reflected both in the potential energy of the whole molecule, in the bond energies, and in the interatomic distances. The C—C distance in benzene is 1.39 Å, instead of 1.46 Å, the mean between the approximately calculated values for a 'theoretical' single C—C link (1.58 Å) and a double link (1.35 Å), and the 'bond order' is not 1.5 as in the theory of simple links but 1.75. The interatomic distances in ethane and ethylene are 1.5 and 1.33 Å respectively, and in these substances it is necessary to assume a certain degree of 'conjugation' between the carbon atoms and a lesser amount along the C—H (donor) bonds. The development of the subject along these lines will doubtless permit of more confident use of thermochemical data to determine the energies of linking in chemical compounds.

In utilizing the above ideas to attempt to elucidate a photochemical mechanism it is first decided on the spectral and bond-energy evidence whether it is likely that the primary effect of the light is to produce excited molecules or atoms or radicals by dissociation. The possible energy states of the products may also be indicated. A reaction scheme is then set up whose total effect accounts for the observed quantum efficiency and kinetics, and which is not improbable on theoretical grounds. The smooth fulfilment of this programme is usually disturbed by gaps in the evidence, uncertainties, ambiguities, and real complexities in the mechanism such as side or successive reactions. It is remarkable how few photochemical reactions can be said with confidence to be thoroughly explained and understood. The frequent production of atoms or radicals in photochemical reactions leads to secondary chain reactions of complex mechanism. These usually betray their presence by high quantum efficiencies and great sensitivity of the kinetics to inhibitors, or chain-ending substances. Experiments made in presence of air sometimes give oxidation products from the reaction of O₂

with radicals. The following quotation from 'Beilstein' illustrates the complexities often encountered. 'By illumination of a benzene solution of nitrosobenzene there is formed azoxybenzene, nitrobenzene, aniline, hydroquinone, *o*-hydroxyazobenzene, *o*-hydroxyazoxybenzene, iso-*o*-hydroxyazoxybenzene, *p*-hydroxyazoxybenzene, water, resin, traces of amino-phenols and of primary bases non-volatile in steam.' Obviously atmospheric oxidation is here complicating the reaction, which like so many other organic reactions proceeds by a mechanism as yet unknown.

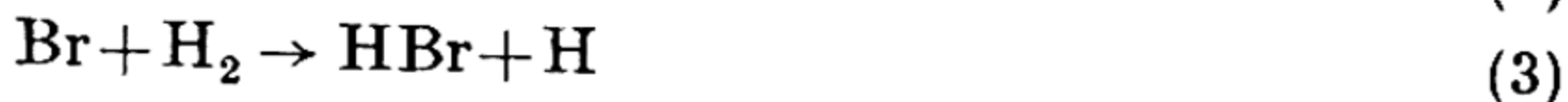
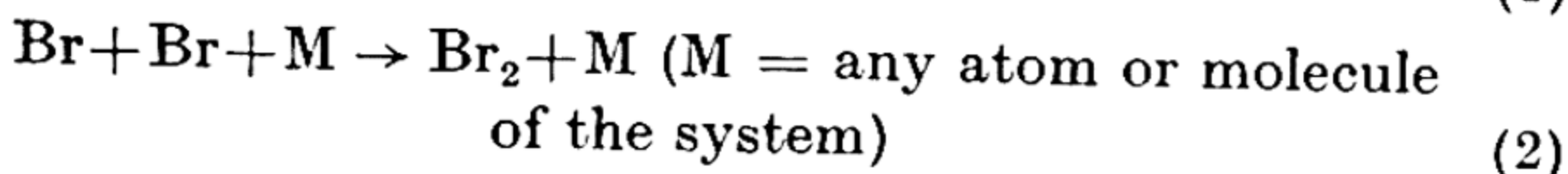
The following is a sketch of the photochemical behaviour of certain systems. Molecular hydrogen is transparent down to 1,150 Å. Fig. 20 shows its energy levels. The permitted transitions giving rise to light absorption are from the ground state to the $^1\Sigma_u$ level at 260 kilo-calories or to the $^1\Pi_u$ level at 283 kilo-calories. These correspond to bands about 1,100 and 1,000 Å respectively. Other transitions are forbidden either because they involve a reversal of electron spin or because the symmetries of the level give no 'transition moment'. The absorption of hydrogen is about the limit of transmission of lithium fluoride, the most transparent material available for the construction of cells. Oxygen (Fig. 21) absorbs weakly near 2,400 Å giving excited molecules ($^3\Sigma_g^- \rightarrow ^3\Sigma_g^+$) at longer wave-lengths where the absorption is banded and dissociates into two normal (3P) oxygen atoms in the shorter-wave continuum. Beyond 2,000 Å a strong band system is observed, where absorption gives $^3\Sigma_u^-$ molecules, and these 'predissociate' to two normal atoms. Beyond 1,751 Å this absorption is continuous, and $O(^3P) + O(^1D)$ is formed by photodissociation. Ozone is formed as the final product in all these regions with a maximum quantum efficiency of 2. Ozone itself absorbs feebly in the red (max. at 6,000 Å) and strongly in the ultra-violet (max. at 2,500 Å) and re-forms oxygen by the process: $O_3 + h\nu \rightarrow O_2 + O$ in which the oxygen atoms and molecules may be in a number of possible levels, while the

kinetics of the photochange are complicated by wall reactions, re-formation of O_3 , etc. Oxygen plays an important role in photochemistry, in photo-oxidations, and as an 'inhibitor' in certain chain reactions, but here the oxygen molecule is not itself the photoactive substance, i.e. the light-absorbing reactant (see below).

In photochemical reactions involving the halogens the primary change is the formation of halogen atoms. The reaction kinetics are determined by the secondary reactions set up. The halogen-hydrogen systems have many important features. The reaction $I + H_2 \rightarrow HI + H$ does not occur owing to the high heat of activation necessary; consequently there is no permanent effect of light on iodine-hydrogen mixtures. The corresponding reaction with bromine has a heat of activation of about 18 kilo-calories, and takes place at measurable speed at about $180^\circ C$. The reaction kinetics have the form

$$\frac{d(HBr)}{dt} = \frac{k_a(H_2)\sqrt{I}}{\sqrt{p}\left(1 + k_b \frac{(HBr)}{(Br_2)}\right)}$$

The rate has the peculiarity of being proportional to the *square root* of the intensity I of the light absorbed, and inversely as the root of the total pressure p . A complete interpretation is given by the mechanism



with the additional assumption that almost all the Br atoms are used up by reaction (2), so that we can write

$$I = \frac{1}{2}k_2 p(Br)^2.$$

As the rate of formation of H atoms must equal their rate of disappearance, we have

$$k_3(\text{Br})(\text{H}_2) = k_4(\text{H})(\text{Br}_2) + k_5(\text{H})(\text{HBr}),$$

and for the rate of formation of HBr

$$\frac{d(\text{HBr})}{dt} = k_3(\text{Br})(\text{H}_2) + k_4(\text{H})(\text{Br}_2) - k_5(\text{H})(\text{HBr}).$$

Eliminating (Br) and (H) between these equations, it follows that

$$\frac{d(\text{HBr})}{dt} = \frac{2k_3(\text{H}_2)\sqrt{(2I)}}{\sqrt{(k_2p)}\left(1 + \frac{k_5}{k_4} \frac{(\text{HBr})}{(\text{Br}_2)}\right)},$$

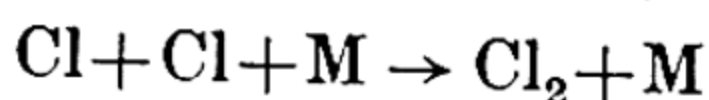
in agreement with the experimental kinetics. The *thermal reaction* between hydrogen and bromine follows an identical mechanism, except that the bromine atoms are produced by thermal dissociation (between 200 and 300° C.)

In the photochemical reaction of chlorine with hydrogen the reaction corresponding to (3) has a low heat of activation (≈ 6 k. cal.) and thus takes place freely at ordinary temperatures. Reaction (4) has a still smaller activation energy. The result is a repeating chain mechanism of these two reactions, giving a very high quantum efficiency (up to 5×10^5) under suitable conditions. The reaction is explosive in intense light. Though the essential features of the reaction are simple, the kinetics are complicated and also exceedingly difficult to establish experimentally. This is because they are determined by the chain-‘ending’ process, which is very dependent on the presence of ‘inhibitors’. For pure mixtures,

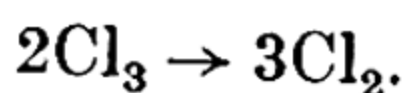
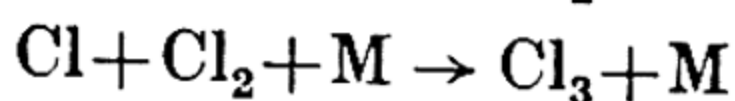
under ordinary pressure conditions, $\frac{d(\text{HCl})}{dt} = k(\text{H}_2)I$, the

rate being proportional to the light absorbed. These kinetics indicate a chain-ending process: $\text{Cl} + \text{wall} \rightarrow \frac{1}{2}\text{Cl}_2$; a supposition in agreement with the observation that the rate is smaller in vessels of greater surface to volume ratio. When the chlorine pressure is high and that of the hydrogen low,

however, the kinetics become $\frac{d(\text{HCl})}{dt} = \frac{k'(\text{H}_2)\sqrt{I}}{(\text{Cl}_2)}$, owing to a different chain-ending process, either,



or,



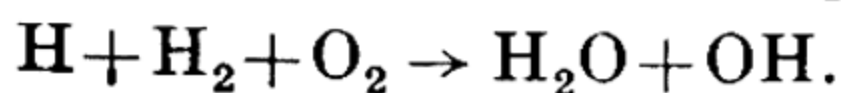
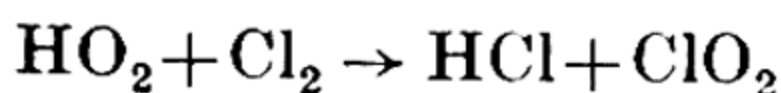
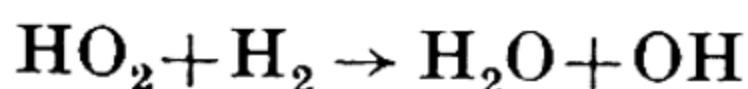
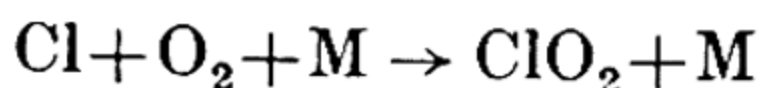
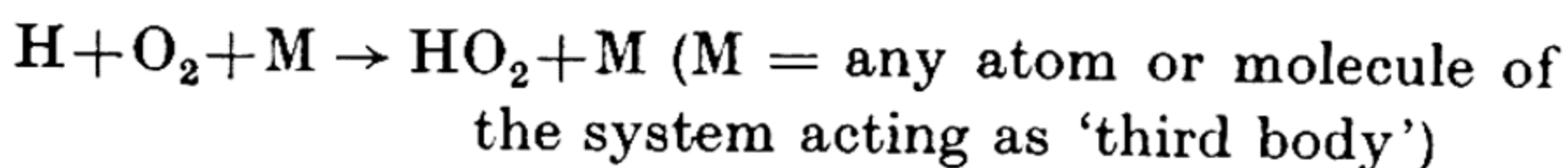
The above results apply only to reacting systems freed from impurities by extraordinary precautions, including purification of the chlorine by fractional distillation, heating the whole apparatus with chlorine to destroy nitrogenous substances (incredibly minute quantities of which inhibit the reaction through the chain-ending properties of NCl_3) and the avoidance of tap-lubricants and other sources of contamination. Without these precautions the photochemical rates are irregular and generally useless for theory. The inhibitor whose effect has received the most study is oxygen. Experimentally it is found that the rate of formation of HCl is given by the expression:

$$\frac{k_1 I[\text{H}_2][\text{Cl}_2] + k_2[\text{O}_2]}{[\text{H}_2][\text{O}_2] + k_3[\text{Cl}_2]}.$$

The oxygen is slowly removed as water by a 'photosensitized' reaction whose quantum efficiency is given by

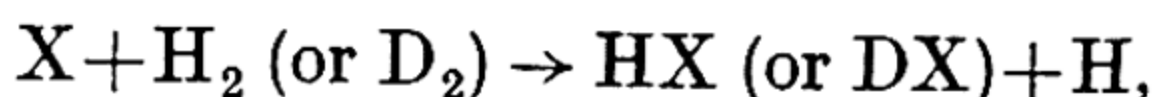
$$\frac{2[\text{H}_2]}{[\text{H}_2] + 3[\text{Cl}_2]}.$$

These kinetics are in harmony with the following hypothetical reactions added to the uninhibited hydrogen-chlorine reactions:



That the molecule HO_2 is formed seems certain from experiments on the effect of oxygen on the photochemical decomposition of HI , where H atoms are formed, but the above scheme is incomplete as it does not provide for the fate of the OH radicals and ClO_2 molecules. So far no way has been found to elucidate these secondary reactions more fully.

The photochemical reaction of chlorine with deuterium is about one-tenth as fast as that with hydrogen under identical conditions. This is attributed to the larger heat of activation of the reaction which controls the kinetics of all the halogen-hydrogen reactions, namely



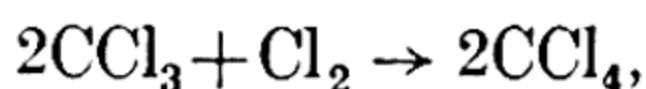
where X is a halogen atom. Such differences of activation energy arise from the differences of vibrational zero-point energy of hydrogen and deuterium, owing to their equal force constants and different masses.

Other photochemical halogenations are also characterized by complex mechanisms. The photoformation of carbonyl chloride involves the intermediate radical COCl which can decompose spontaneously or by reaction with a chlorine atom, or may form COCl_2 by reaction with a chlorine molecule, thereby initiating a 'chain'. The simplest photochemical organic substitution reaction is the chlorination of chloroform.

The observed kinetics are:

$$\frac{d[\text{CCl}_4]}{dt} = k\sqrt{I[\text{Cl}_2]}.$$

This is explicable by a reaction of CHCl_3 with Cl atoms to give HCl and the radical CCl_3 . The latter reacts with Cl_2 to give CCl_4 and a further Cl atom which initiates a 'chain'. The 'chain-ending' process must be assumed to be



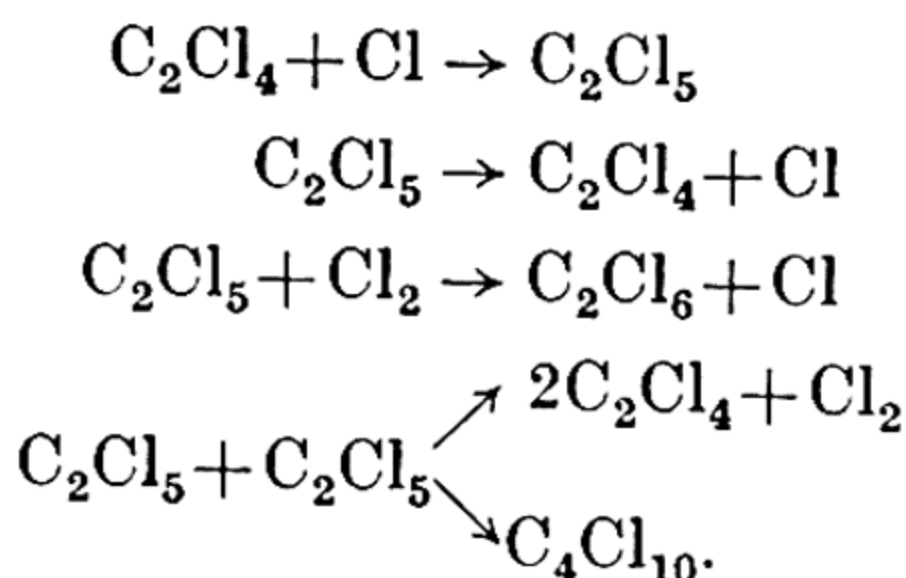
since no other process will reproduce the experimental kinetics. Other substitution reactions are the photo-

chlorinations of methane, acetic acid, and toluene. All these are chain reactions involving chlorine atoms and organic radicals, and they show strong inhibition by oxygen which acts by removing the organic radical participants in the 'chains'.

The simplest photochlorination of an additive nature is the reaction of chlorine with tetrachloroethylene. The experimental kinetics are

$$\frac{d[\text{C}_2\text{Cl}_6]}{dt} = k\sqrt{I}[\text{Cl}_2].$$

The quantum efficiency is high, and besides the chief product C_2Cl_6 some C_4Cl_{10} is also formed. The following scheme is in agreement with the kinetics:



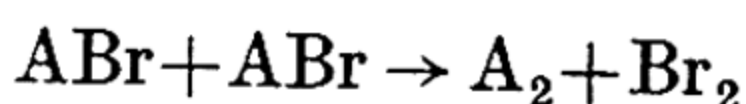
In contrast to this is the photochlorination of ethylene itself. The kinetics are simply:

$$\frac{d[\text{C}_2\text{H}_4\text{Cl}_2]}{dt} = kI.$$

This difference arises only from a difference of chain-ending process. The square-root light-intensity relationships above come from bimolecular recombinations of radicals; the first power relationship for the ethylene reaction must be due to a chain-ending process of a single atom or radical reacting with an ethylene molecule, or to reactions occurring on the walls of the vessel.

Photobrominations of organic molecules such as cinnamic acid (see Appendix V) sometimes appear deceptively simple. In presence of dissolved air the solutions give reproducible

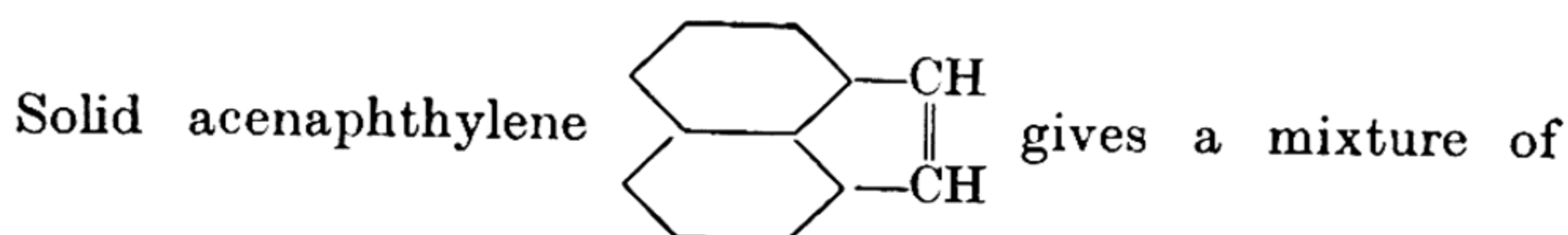
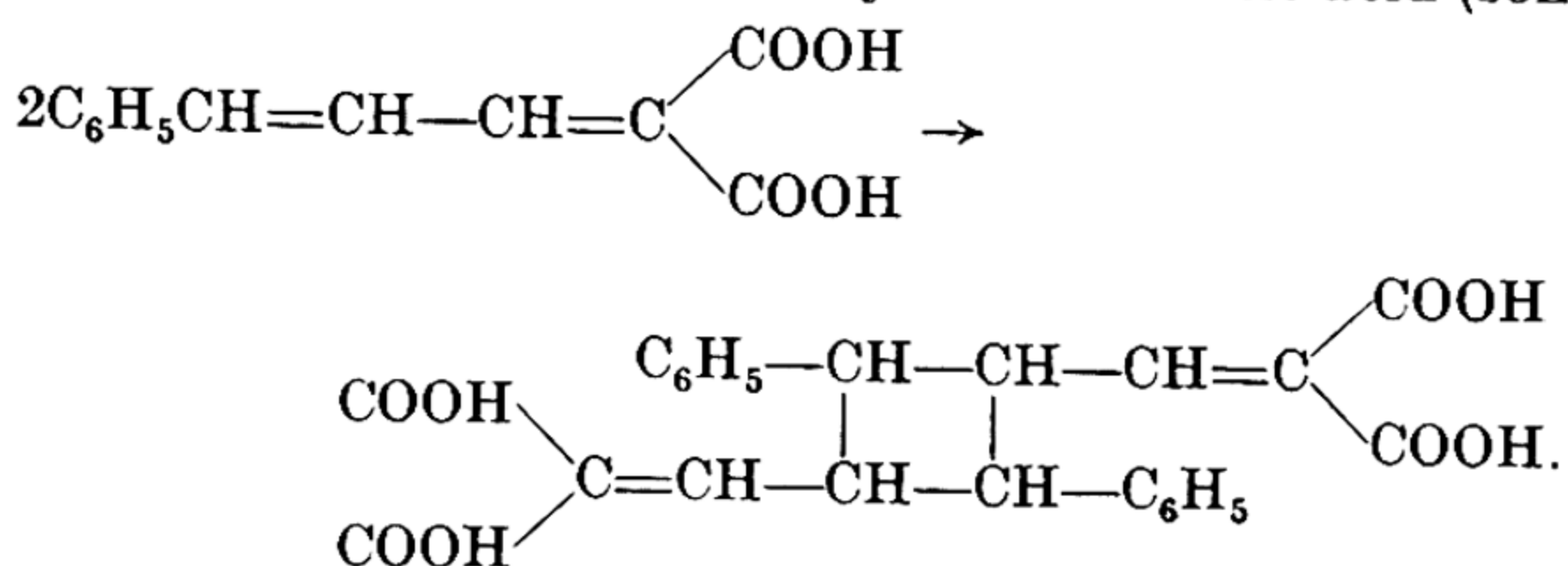
kinetics, the rate varying as the square roots of the light intensity and the light absorbed by the bromine and being independent of the organic reactant concentration. Elimination of oxygen, however, leads to much faster rates with possibly different kinetics which are experimentally difficult to determine. A feature of brominations such as the above is the side-production of dimeric molecules evidently formed by the elimination of halogen atoms from two colliding radicals, as



where A = cinnamic acid. In presence of air a large uptake of oxygen occurs during the photobromination with formation of oxidation products. Though the details of these reactions still remain obscure, it is clear that the first effect of bromine atoms formed in the primary process by the light is to attack the double bonds of the molecule to give radicals as $A\text{Br}$. The radicals are further brominated to the dibromide by collision with Br_2 molecules, liberating more bromine atoms and setting up reaction chains. These chains are interfered with and terminated by reaction of the radicals either with oxygen molecules or with one another. Besides sensitizing photo-oxidation processes as above, halogens sometimes photo-sensitize cis-trans changes, e.g. in presence of light and Br_2 maleic ester changes to fumaric ester. This effect again occurs through the formation of intermediate radicals with one atom of bromine attached to the double bond whereby the resistance to rotation of this bond is greatly reduced. Such reactions may be accompanied by a certain amount of photo-oxidation and of dimer formation.

Saturated hydrocarbons are very transparent to ultra-violet light and show little change. Ethylene exposed to wave-lengths shorter than $1,250 \text{ \AA}$ gives a polymer together with hydrogen, acetylene, and other products. Benzene dissociates below $2,000 \text{ \AA}$ to give the phenyl radical and a hydrogen atom. Absorption by molecules with double bonds

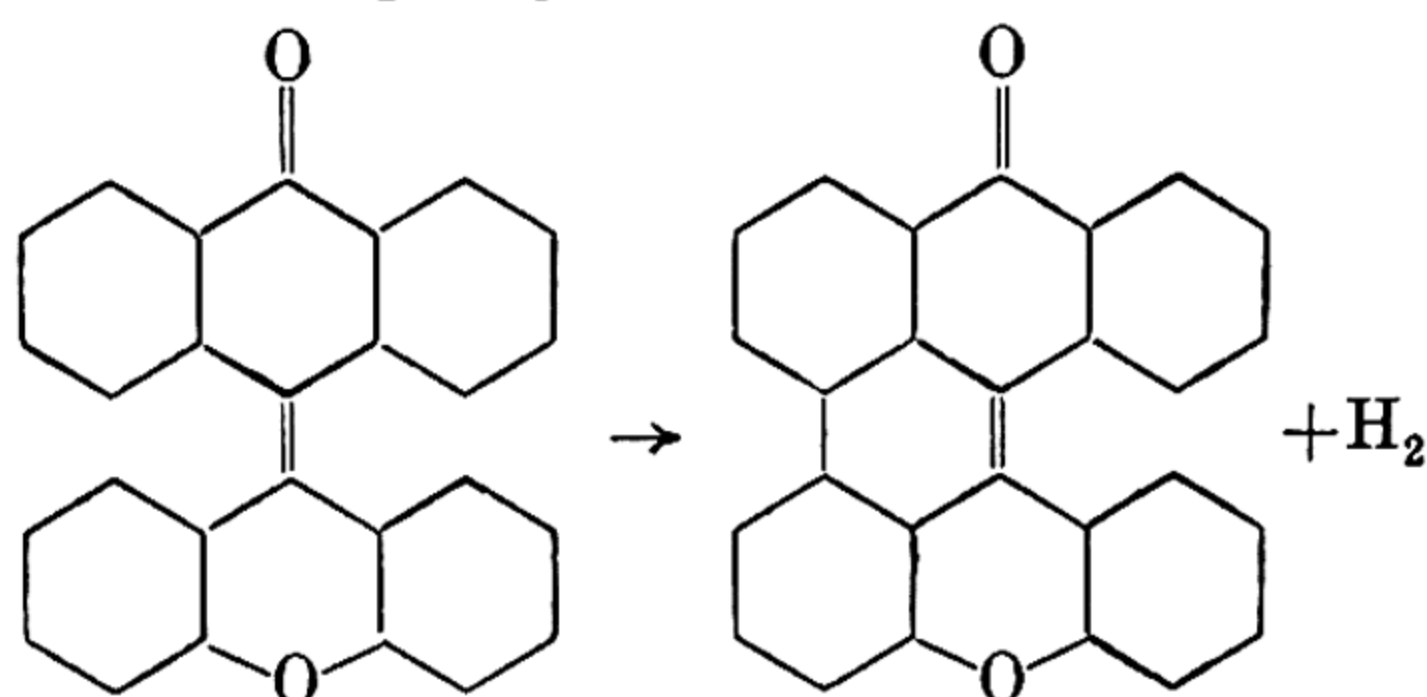
often leads to geometrical isomerization, e.g. benzantialdoxime changes to the *syn* compound, *trans* stilbene to *cis*, while azobenzene (*trans*), cinnamic acid, fumaric and maleic acids take up photostationary states of *cis-trans* forms. The equilibrium conditions are complicated since each component is photoactive, having different absorptions (p. 124) and different specific rates of change, the latter being determined by the (small) heat of activation necessary for the excited link to twist round. The overall quantum efficiencies of these changes are therefore less than unity. In the solid state, or in some cases in concentrated solution, dimers with a cyclobutane ring are formed, e.g. with cinnamylidene malonic acid (solid),



two isomeric dimers, while solid cinnamic acid forms two dimers, α -truxillic or β -truxinic acids, depending on the crystalline state of the acid. Stilbene, acenaphthylene, cumarin, and some other molecules also dimerize photochemically in strong solutions; being fluorescent substances they have long-life excited states which allow the bimolecular reaction to occur. Dimerization by light is also facilitated by certain catalysts; uranyl salts give complexes in certain instances so that two or more molecules are held in juxtaposition ready to react in light, while halogens allow some photochemical dimerizations of ethylenic substances to take place as a 'chain-ending' reaction between intermediate

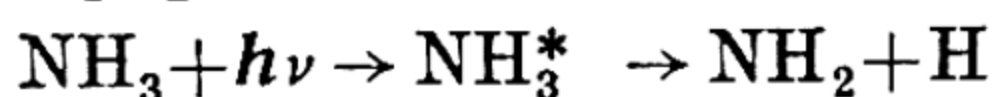
radicals with one halogen atom attached to the double bond which are formed in photohalogenation.

Some highly conjugated organic molecules lose a molecule of hydrogen photochemically with the production of a new link between the rings, e.g. the following xanthylene anthrone:

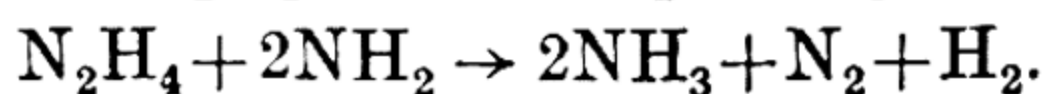
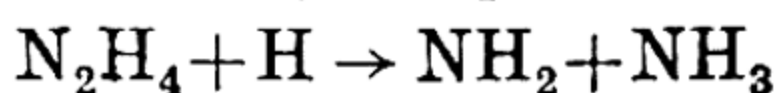
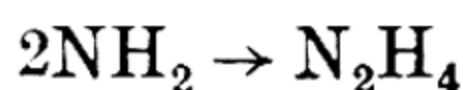
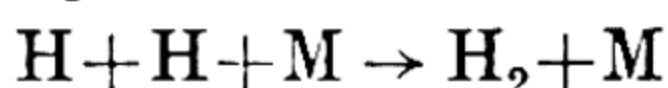


The NO_2 molecule absorbs in the visible region and fluoresces when excited by wave-lengths longer than $3,900 \text{ \AA}$. Excited NO_2 molecules are formed at the longer wave-lengths which lose their energy by radiation or at higher pressures by collisional deactivation. At shorter wave-lengths the molecule dissociates into $\text{NO} + \text{O}$; no fluorescence is observed and the quantum efficiency is 2. The spectrum becomes diffuse at higher pressures near $3,700 \text{ \AA}$, indicating that the dissociation process is one of 'induced predissociation'.

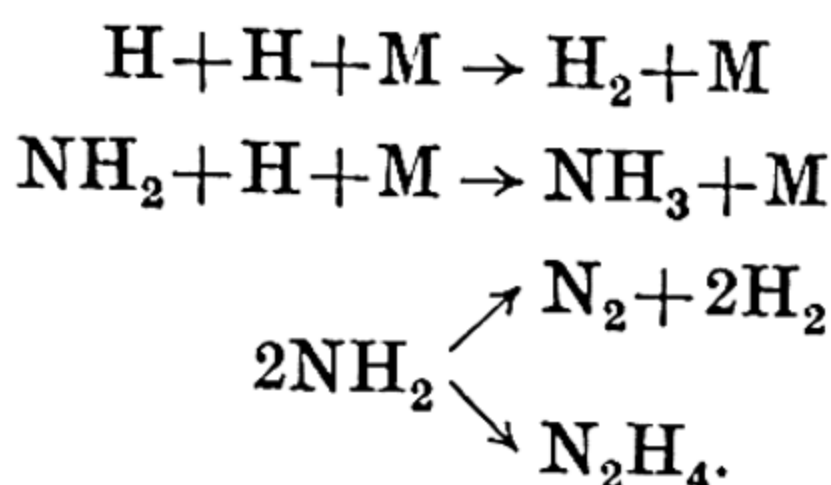
Ammonia has a spectrum of diffuse bands in the region near $2,000 \text{ \AA}$ indicating 'predissociation', probably



(possible at $Nh\nu > 112 \text{ k. cal.}$). The final products are N_2 , H_2 , and a little hydrazine N_2H_4 . A puzzling feature of the reaction is the low quantum efficiency of decomposition (about 0.2), and different investigators have proposed discordant mechanisms. One mechanism invokes a back reaction re-forming NH_3 , the secondary reactions being:

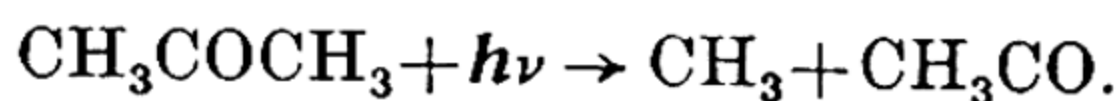


Another is as follows:

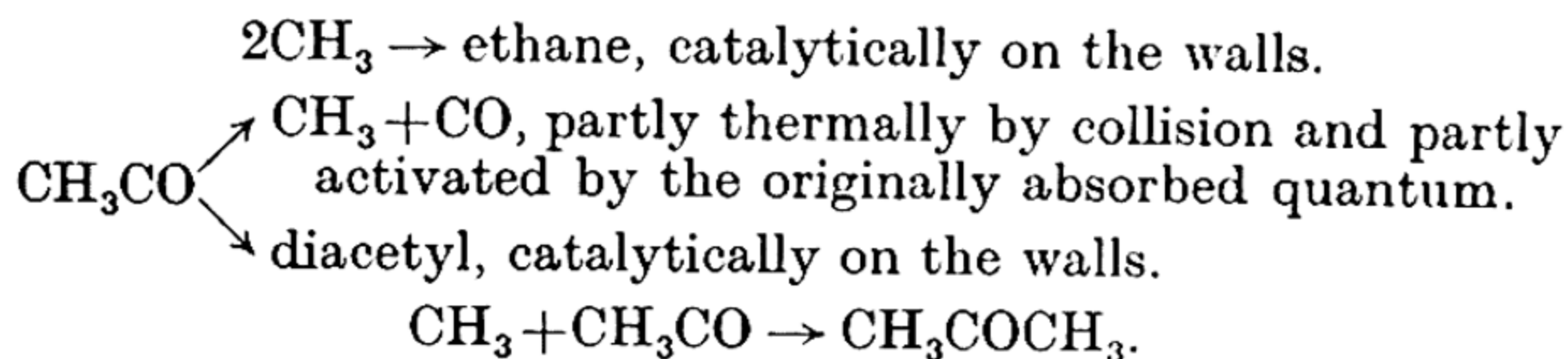


It is probable that wall reactions play a part in the secondary reactions, and further work is required to decide between the possibilities. Aliphatic amines also photolyse giving complex products, but the primary reaction seems to be the splitting of a hydrogen atom from the nitrogen.

Acetone has an absorption band about 3,000 Å which is difficult to interpret; it appears superficially largely continuous, but it may be that a large part at least of the continuum is due to close packing of a fine structure of rotation lines. Whether the primary mechanism be photodissociation, 'normal' or 'induced' predissociation, there is little doubt that the first step is



This photoreaction in the gaseous state also has a low quantum efficiency (about 0.2). The following secondary changes are probable:



These processes explain the existence of CH_3 radicals during the photochange (as shown by reaction with metallic mirrors), the formation of small amounts of diacetyl, and the low over-all quantum efficiency (about 0.2). In presence of iodine, which removes CH_3 radicals as CH_3I , the quantum efficiency rises to unity, the back reaction being prevented. The quantum efficiency also becomes unity at 100° C,

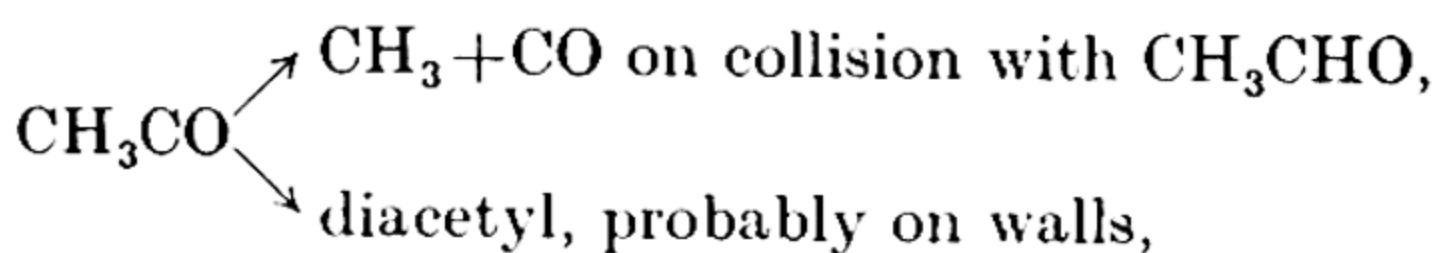
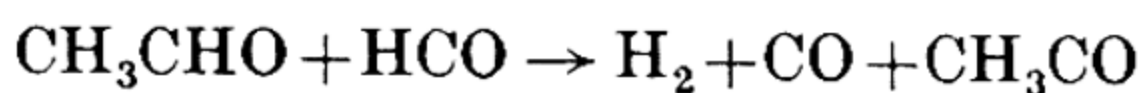
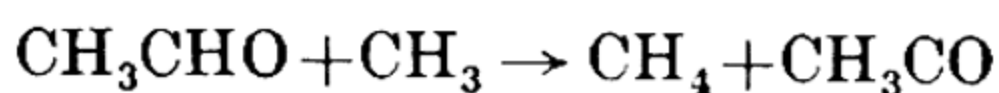
probably due to the decreasing stability of the CH_3CO radical, which decomposes before taking part in the back reaction. It will be noted that it is not assumed that CH_3 radicals combine in the vapour to give ethane since no ethane is found in other photoreactions (e.g. acetaldehyde) where CH_3 radicals are present in quantity. This reaction evidently has a high heat of activation.

The ammonia and acetone photoreactions not only resemble one another in their unexpectedly low quantum efficiencies for their changes in the gaseous state, but also in the suppression of the change in the liquid or dissolved state. The most probable explanation of this is due to Franck and Rabinowitch. The liquid state of matter is at least as closely akin to the solid state as it is to the gaseous. The molecules are so close together that the motions they execute are more of the nature of vibrations than translations. If a molecule dissociates in a liquid, the products are so hemmed in by other molecules that they are forced to collide with one another a great number of times before they escape, and during this period they have a great chance of recombining again.

The lower aliphatic aldehydes have been the subject of extensive investigation photochemically. Like the ketones they absorb near 3,000 Å. Formaldehyde has a fine-structured region on the long-wave side of the band, followed by a diffuse region and then by a continuous one. As the homologous series of aldehydes is ascended, the diffuse and continuous regions become more prominent. Fluorescence is observable at the long-wave end of the bands. The nature of the primary reaction is not clearly indicated by the spectral evidence. Study of the quantum efficiencies and of the final products, together with considerations based on the (very roughly) calculated values of the bond energies of the links, seem to show that the reaction



occurs at longer wave-lengths, while free radical formation, $R+CHO$, occurs at the shorter. Where R is a long chain, a peculiar decomposition into an olefine and acetaldehyde or acetone occurs with aldehydes or ketones. The photodecomposition of acetaldehyde has been the subject of much investigation. The physical process following the light absorption is the passage of an electron from a 'lone-pair' on the oxygen atom to an 'antibonding' molecular orbital. As the final molecular cleavage is not between the C and O, considerable alterations in molecular structure must occur before decomposition. The quantum efficiencies of decomposition vary with the conditions, lying between 0.2 and 0.95 (calculated on the CO formed). In addition to the main products, small quantities of hydrogen, diacetyl, glyoxal, formaldehyde, and a liquid 'polymer' are also formed in amounts varying with temperature and wave-length. No ethane is detectable, however, showing that the reaction between two CH_3 radicals, in the gas phase or on the walls, does not occur appreciably. The following reactions are probable:



together with the possible formation of hydrogen atoms and their subsequent reactions, and bimolecular and other reactions of the HCO radical. At elevated temperatures the above steps become a repeating long-chain mechanism involving the first and third reactions, and the rate becomes proportional to the square root of the light intensity. This indicates that the chains are ended by bimolecular recombination of radicals, probably: $CH_3 + CH_3CO \rightarrow CH_3COCH_3$; the amount of acetone formed, of course, being very small. The 'half-life' of the radicals taking part in the long chains

can be found by 'sector' experiments, as can the chain mechanisms of all photochemical reactions which are proportional to the square root of the light absorbed. The basis of the theory of this is as follows. Imagine an opaque rotating disk with one quadrant removed placed in the path of the light. At high rates of revolution the radicals will not have time to recombine in the periods of darkness. If the original light is of intensity $4I$, with the disk it will be reduced to I . The observed rate will be proportional to \sqrt{I} . At low disk speeds, however, the radicals combine during the long periods of darkness and the effect will be that of light of intensity $4I$ acting for $\frac{1}{4}$ of the time; i.e. the rate will be proportional to $\frac{1}{4}\sqrt{4I}$ or to $\frac{1}{2}\sqrt{I}$. The intermediate disk speed where the rate changes from one value to the other gives roughly the average life of the radicals. In this way, for example, the rate controlling radicals in the above system are found to have a life of about 0.5 sec. at 200° C. and 20 cm. pressure, whence it may be deduced that for the first reaction (the slower of the two) one collision in every 3×10^7 of the methyl group is effective, and that the activation energy has an upper limit of about 16 k. cal.

In addition to the 'mirror' method other ways are available for the detection of radicals, and also for hydrogen atoms, suspected of being present in photochemical or thermal reactions. Oxygen, for example, combines with these bodies, but its effect on chain reactions is sometimes of a complicated nature. Nitric oxide (an odd-electron molecule) is more useful; it appears to remove radicals very efficiently. For example, when added to acetaldehyde decomposing photochemically at high temperatures, its suppression of the chain reactions is shown by the reduction of the quantum efficiency to unity and the change of the rate law from proportionality to \sqrt{I} to I . The ortho-para hydrogen conversion is catalysed by atoms or radicals; it has the disadvantage, however, of being rather slow, so that if the reaction chains are rapid

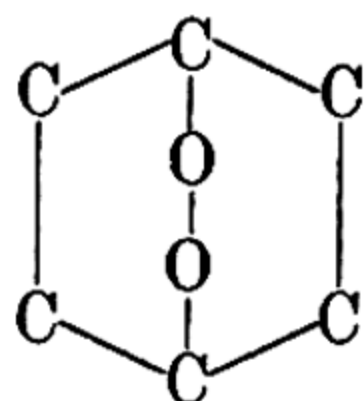
the atomic concentration may be insufficient to bring about measurable conversion. A more direct method of elucidating chain mechanisms is to add atoms or radicals to the system. H atoms from the photochemical decomposition of HI, methyl radicals from acetone or by heating azomethane, may be so employed. In this way information is accumulating on chemical processes which have refused to yield to ordinary kinetic investigations.

Bichromates under the influence of shorter-wave visible light oxidize organic compounds such as alcohol, gelatine, etc., and this forms the basis of various technical processes of photoreproduction. The mechanism is obscure, but a pH more acid than 7 is necessary, as the CrO_4^- ion is inactive and behaves as an inner filter. Complex oxalate ions are photochemically sensitive, particularly ferri-, cobalti-, and mangan-oxalates, and decompose giving CO_2 and an ion of lower valency. Potassium ferri-oxalate or ammonium ferri-citrate is used in the making of 'blue prints'. Uranyl oxalate ions with excess oxalic acid decompose in a different way; CO and CO_2 are given off and the uranyl valency state is unchanged. This reaction is used for ultra-violet actinometry (p. 284). The system $\text{Fe}^{++} + \text{I}_3^- \rightleftharpoons \text{Fe}^{+++} + \text{I}^-$ comes to a thermal equilibrium in the dark. Under the influence of light absorbed by the I_3^- a photoequilibrium is attained more to the right-hand side of the equation. Thionine and ferrous ions in a phosphoric acid solution form a similar but more sensitive photoequilibrium; the dye is reduced to colourless substances in light and is reoxidized back by the ferric ions formed when left in the dark. If suitable reversible electrodes could be found, reactions of this type could be used to transform light energy into electricity.

In photo-oxidations of organic compounds by oxygen the organic compound absorbs the light, and the oxygen reacts as the molecule O_2 . The aromatic hydrocarbon rubrene, which is bright red in colour, takes up oxygen when exposed in

benzene solution to light, forming a colourless peroxide be-

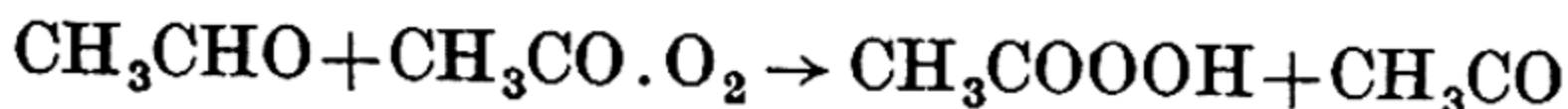
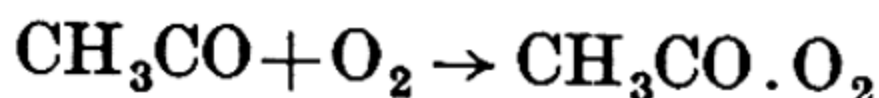
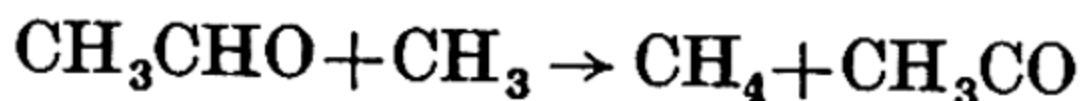
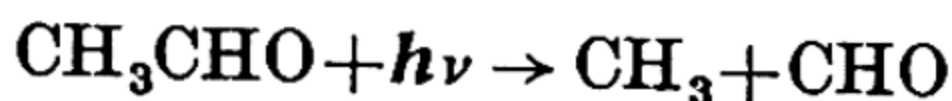
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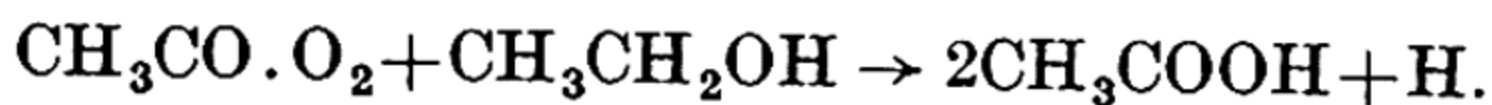
, and having the

peculiar property of reverting to the hydrocarbon with evolution of oxygen on heating. Anthracene forms a less stable similar peroxide when exposed to air and light in CS_2 solution, and the photo-oxidation of benzene in ultra-violet light is probably due to a similar peroxide. The oxygen molecule may be attached by π electron interaction instead of valencies. The formation of these peroxides is not an entirely simple reaction. Dissolved oxygen quenches the fluorescence of these hydrocarbons in solution, and comparison of the quenching and of the photo-oxidation shows that collisions between oxygen and excited hydrocarbon molecules which result in fluorescence quenching do not all lead to stable peroxide formation. It seems likely that the first effect is the attachment of the oxygen to the hydrocarbon by a feeble linkage only, giving a complex which may dissociate again or proceed to further reaction, and in more concentrated solutions dimer radicals are formed which may either dissociate again, react with oxygen to give peroxide, or (in the case of anthracene) also form stable dimer molecules. When reducing agents are added to systems of the above kind 'photo-sensitized oxidation' often occurs, i.e. the coloured substance absorbs the light but the reducing agent is oxidized. There is little doubt that here reactive intermediate peroxides formed photochemically between the coloured substance and oxygen, instead of dissociating or forming stable oxidation products, oxidize the reducing agent leaving the coloured substance effectively unchanged at the end of the reaction (p. 164). Acetaldehyde and oxygen in ultra-violet light gives peracetic acid; the kinetics indicating a chain reaction whose rate is proportional to the square root of the light intensity, directly

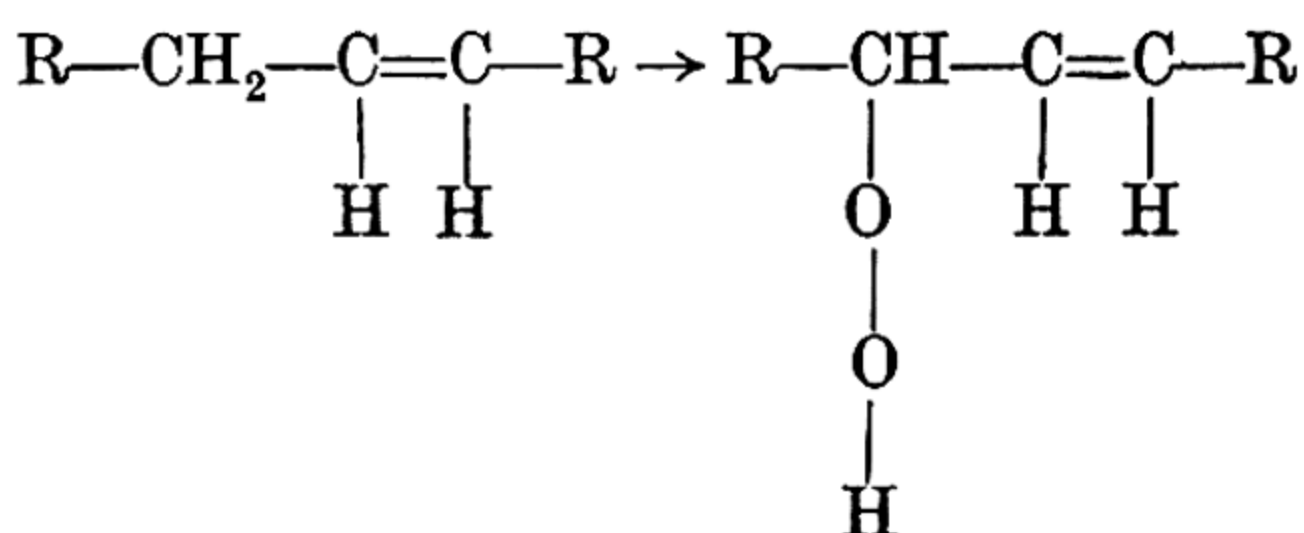
as the aldehyde concentration, and independent of the oxygen concentration. In addition, quantities of diacetyl peroxide are formed. The following steps seem likely when all the known facts are considered:



In presence of alcohol the chain mechanism is inhibited and the rate becomes proportional directly to the light intensity. This is explicable if the final reaction above is replaced by



The kinetics are insufficient to determine the right-hand side of this equation, or to prove that the above scheme is the only correct one. More work on the side products of the chain and on their variation with conditions is necessary for a completely satisfactory solution. It may be pointed out that in the above reaction, because of the peculiar kinetics, the inhibiting effect of alcohol depends on the light intensity. Photo-oxidation by atmospheric oxygen is of importance technically in problems of the drying of oils in paint and their subsequent deterioration, in the fading of certain dyes, and in the action of light on rubber. The fading of dyes in light is due to a number of different types of reaction, of which photo-oxidation is most important for basic dyes, while dyes on cotton are reduced by reaction with the fabric. Unsaturated oils, fats, and rubbers photo-oxidize by chain mechanisms which are inhibited by the presence of 'anti-oxygens' such as hydroquinone. The stages are not understood, but involve the formation of hydroperoxides with the oxygen attached to a carbon atom next to one having a double bond:



These further react in a complicated way giving derivatives of ethylene oxide, ketones, and products derived by polymerization and secondary oxidation together with some splitting of the molecule at the double bond. Certain pigments such as ZnO and TiO₂ absorb the near ultra-violet and photosensitize drying oils, etc., so that destructive reactions involving oxidations are set up, the nature of which remain to be discovered.

Since the amount of a photochemical change depends on the amount of light absorbed, any variations in absorption are reflected in differences of photochemical rate. Such variations may arise from the use of polarized light and molecules oriented in crystals. An interesting example is solid *o*-nitrobenzaldehyde, which changes in light into *o*-nitrosobenzoic acid. In the early stages of the change the nitroso compound is produced in the green monomeric form in solid solution in the nitro aldehyde; later it forms a new solid phase of the colourless dimeric substance. Owing to the dichroism of the nitro aldehyde crystals, thin specimens absorb plane-polarized light unequally in different directions; hence the rate of photochange depends on the orientation of the light vector to the crystal. This change has a quantum efficiency of about 0.5. Similar variations of rate with orientation are shown by the photodimerization of thin crystals of cinnamylidene malonic acid in plane-polarized light. The term *photodichroism* is sometimes used to cover examples of similar effects of plane-polarized light on oriented molecules in cases where the photoproduct becomes coloured and partly polarizes transmitted white light in which it is viewed.

Another effect of absorption differences arises from the use of circularly polarized light and optically active substances. The two forms of an optically active substance *d* and *l* have unequal refractive indices, and if they are coloured, different extinction coefficients, to circularly polarized light. The differences are small and difficult to establish experimentally. An example is found in β -chloro β -nitroso α - δ diphenyl butane. A weakly absorbing solution of the racemic mixture of this substance is unequally decomposed by *d* circularly polarized light so that after 90 per cent. decomposition a recognizable excess of one of the optically active forms over the other remains behind.

VII

PHOTOSYNTHESIS IN PLANTS

ON the reaction whereby plants convert solar energy into the potential energy of the materials they build up in their growth depends the whole life on the earth. The mechanism of the process is very complex, and presents many problems of great difficulty. Such facts as have already been established show that it includes peculiar features not observed in simpler photochemical reactions. Though certain coloured bacteria can utilize light in their development, the dominant photosynthetic process is that associated with the *green plants*, and this has naturally received almost all the attention of investigators.

The total radiant energy of sunlight received at the earth's surface is 1–1.95 calories per sq. cm. per minute, depending on altitude, or one horse-power per 10–20 sq. ft. For crop plants in the field a maximum of 2–3 per cent. of this energy remains stored in the plants at the end of the growing season. During that time about 20 per cent. more is actually used in photosynthesis and lost by the respiration of the plant (breathing out of CO_2), the remainder of the energy being dissipated by re-radiation, transmission through the leaves, and the evaporation of water from the plants.

All the carbon of organic matter has been derived by the influence of sunlight through the photosynthetic process from CO_2 , and all the free oxygen in the atmosphere represents part of that liberated in the change. The present geological distribution of carbon of organic matter is roughly:

In living matter and soil, 10^{18} gm.

Coal and peat, 10^{19} gm.

Oil, 2×10^{16} gm.

Shales and other rocks, 4.5×10^{21} gm.

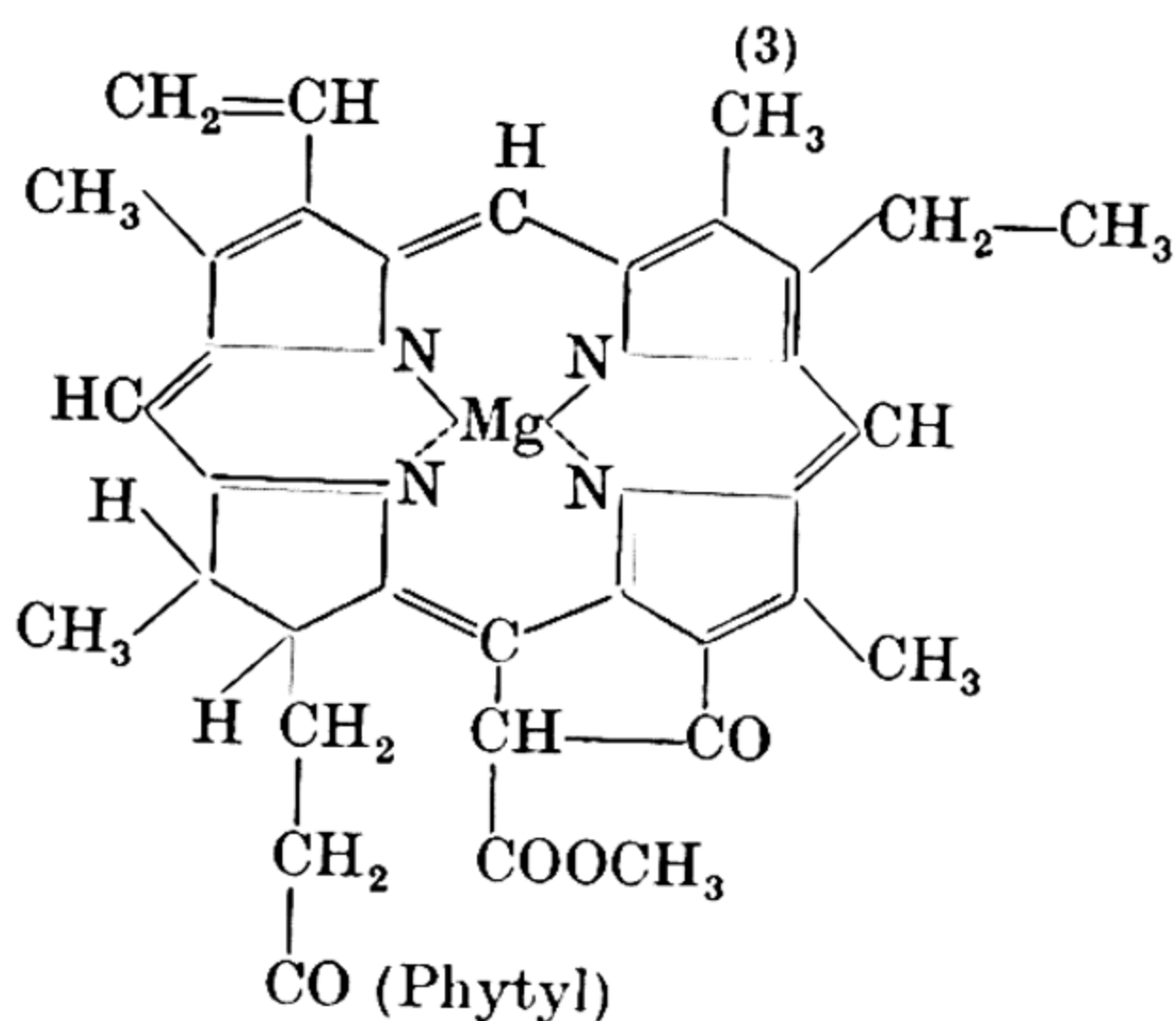
CO_2 in the air, 2×10^{18} gm.

CO_2 in the sea, 4×10^{19} gm.

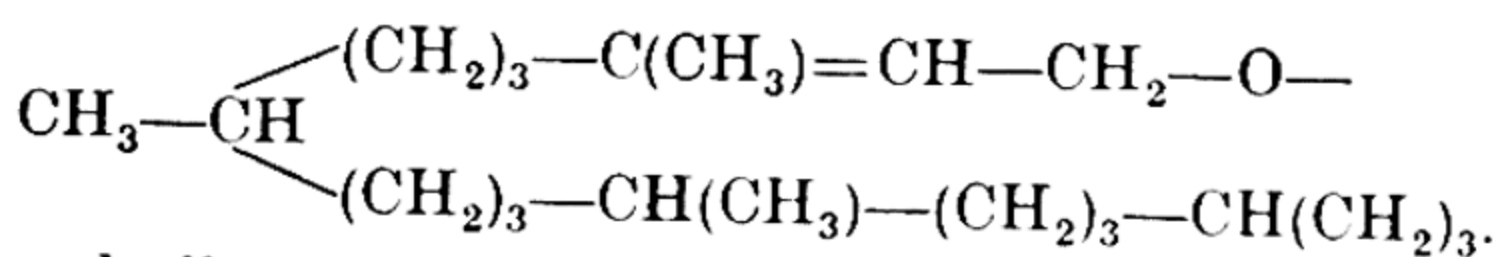
The free oxygen in the air is about 1.2×10^{21} gm., in the sea one hundredth of this, and the remaining 10^{22} gm. has found its way into rock deposits.

It is a very remarkable fact that the CO_2 content of the air is as low as 0.03 per cent. by volume, and on this small percentage the whole body of the vegetable world must contrive to live. Plants have usually developed complex forms of leaves with porous interiors to cope with this problem; the rate of take-up of CO_2 by leaves is as high as by sodium hydroxide solution.

The leaves of green plants contain coloured substances, of which *chlorophyll* appears to be the only one directly concerned in photosynthesis. The constitution of this substance has been investigated by Willstätter and his followers. Two forms have been recognized, chlorophyll *a* and chlorophyll *b*. These are porphyrin derivatives, chlorophyll *a* having the probable structure:



where (Phytyl) is



Chlorophyll *b* differs in having the group $-\text{CHO}$ in place of $-\text{CH}_3$ at position (3). Both substances are soluble in

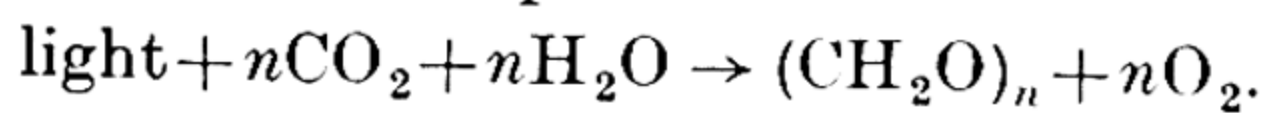
organic liquids, but form colloidal solutions in water. Chlorophylls *a* and *b* exist in the fairly constant proportion of 3 : 1, independent of the nature of the plant and of the action of light or darkness.

Chlorophyll shows two well-defined absorption bands in the visible region. The *a* compound has one peak at 6,600 Å and another at 4,250 Å, while the *b* modification has similar bands shifted somewhat inwards towards the centre of the visible region. It is curious that the compound utilized by plants for absorbing sunlight should take up red and blue light, but not absorb the green region where the radiation is most intense. If chlorophyll did absorb in the green region, however, other factors being what they are, the plant could not utilize the extra energy absorbed, and the leaf might be dangerously heated. Chlorophyll shows a red fluorescence (band 6,500–7,500 Å) which in the leaf varies both with time and with the oxygen concentration. Energy lost in this way is unavailable for photosynthesis.

In order to develop chlorophyll plants need supplies of iron salts; if these are deficient *chlorosis* or chlorophyll lack occurs. The other leaf pigments are mostly carotenoid derivatives, characterized by a chain of 22 CH groups with alternate single and double links, whose functions in the plant are still obscure. They vary in proportions in different plants and afford complex problems of separation by chromatographic technique. The commonest is the yellow hydrocarbon carotene, which exists in more than one allied form and is related to vitamin A. Carotene and its oxidation product xanthophyll vary in proportion during photosynthesis, and although the light they absorb seems not to be utilized in the process they may well play some part in the dark stages later. The leaf pigments may be prepared either by grinding up a few nettle leaves with petrol ether (B.P. 70° C.) containing a little benzene and methyl alcohol, or by soaking the air-dried leaves with acetone containing 20 per cent. water by volume

and shaking with petrol ether containing a little benzene, washing the petrol ether extract cautiously with several quantities of water, and pouring down a 10×1 cm. column of sucrose below which are short layers of calcium carbonate and aluminium oxide. The chromatogram is developed by pouring in more petrol ether-benzene, giving a top zone of light green chlorophyll *b* and a second zone of more bluish green chlorophyll *a*, while the yellow xanthophyll is retained by the CaCO_3 and the carotene by the Al_2O_3 . These zones are rendered even more visible by their fluorescence in ultra-violet light.

Photosynthesis consists in the utilization of light energy by plants for building up organic materials from inorganic ones, and occurs in the green parts of plants, i.e. being usually confined to the leaves. The reactions occurring are very complex. The main one is the conversion of carbon dioxide into the woody structure of the plant. Each leaf has many minute *stomata* or holes communicating with internal channels to secure high efficiency in obtaining CO_2 . Nitrates drawn up from the soil are also photosynthetically converted in the leaf into amino-acids and proteins to form the 'protoplasm' of the plant, which needs constant renewal during life. The major part of the food production of the plant is effected by the red-orange rays, but the blue-violet region is essential for the control of water-evaporation through the leaves and for mechanisms *regulating* growth. Chemically the carbon assimilation process can be represented as



The volume of oxygen liberated very closely agrees with the volume of carbon dioxide taken up when allowance is made for the respiration of the plant. The respiration, which goes on in darkness and in light, absorbs oxygen and liberates carbon dioxide, again in the molar ratio 1 : 1. The first easily recognizable product corresponding to $(\text{CH}_2\text{O})_n$ in higher plants is starch, which consists of branched and unbranched

chains of 100–2,000 glucose residues, but by special methods (see below) the existence of water-soluble material of molecular weight about 1,000 containing —OH and —COOH groups has been proved. No free formaldehyde or similar simple substances, nor sugars, have been identified as the first or early products of photosynthesis. (Sugars are formed subsequently by the plant in the dark.) This uncertainty and complexity of the first detectable product, though affording scope for the imagination, is a serious handicap to the development of useful theories of the reaction mechanism. It has so far not been possible to discover experimentally the substances formed in earlier stages of the process, which cannot be conceived as occurring in one step. When chlorophyll is extracted from the plant it fails to reproduce its photosynthetic properties, so that simplification of the working conditions has been unrealizable. It is necessary, therefore, to experiment with actual plants, and the interpretation of observations is greatly complicated by the unknown and inextricable relations of the numerous factors involved. If the kinetics of the reaction are to be studied in the conventional way, it is first necessary to obtain conditions of known and uniform light absorption, and this cannot be secured in any living organism owing to the complicated arrangement of the chlorophyll in *chloroplasts* on the non-homogeneous plant structure. The chloroplasts are often disk-like and change their orientation under different conditions of light intensity, altering the amount of light absorbed. The nearest approach to a solution of this difficulty is found in the use of thin layers of certain unicellular aquatic plants such as *Chlorella*. The same complexity affects the determination of other experimental variables such as carbon dioxide uptake in terms of diffusion. The holes, about 0.01 mm. diameter (*stomata*), through which carbon dioxide gains access to the inner part of the leaves of terrestrial plants, alter in size under different conditions of light intensity, water supply, etc. However, when these com-

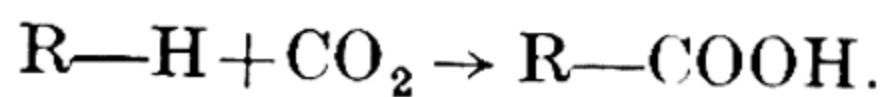
plications are eliminated as far as possible, it is found that at very low light intensities ($< \frac{1}{50}$ sunlight) or low carbon dioxide concentrations the rate of photosynthesis is proportional to these quantities, but becomes independent of them when they are large. At the same time the effect of temperature becomes large at high intensities or carbon dioxide concentrations while for low values of these the rate is independent of temperature. The conclusion may then be drawn that at the higher values of the above two variables the rate ceases to be dependent on them, and instead becomes governed by a slow *thermal* reaction in the plant. It is at this point that special difficulties arise. In a simpler system the factors influencing the rate could be separated, and the reaction studied when controlled by the slowest under the experimental conditions. The plant, however, like all living beings, has a self-regulating mechanism whereby the alteration of any one factor alters all the others to non-measurable extents. The refinement of observational data necessary for a clearer insight into the reactions tends to elude the investigator. The best experimental technique for following photosynthesis is to keep the plant in a stream of air or nitrogen containing CO_2 and to determine either the oxygen evolved with a dropping-mercury electrode, or the CO_2 by infra-red absorption or its 'dew-point' at low temperatures.

Attempts have been made to measure directly the actual quantum efficiency of the process. The most reliable values indicate efficiencies approaching 0.1. Photosynthesis can occur at as long a wave-length as 7,000 Å, corresponding to 38 k. calories per mole. The reaction $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2$ requires 110 k. calories per mole. The reaction therefore must be complex, and needs at least three, if not four, quanta. The photosynthetic process does not fall far short of the maximum possible efficiency if this is taken into account. A problem has been how to explain the participation of several quanta in the fixation of one molecule of

carbon dioxide. Nothing analogous to this has been observed in simple photoprocesses. The probable explanation is found in the hypothesis of the *photosynthetic unit*. In experiments using intermittent light flashes it is found that the intensity at which the reaction rate becomes independent of this variable is higher than for continuous light. This may be explained by the functioning of thermal reaction stages in the dark periods between the flashes. The amount of photosynthesis compared with the chlorophyll effecting it leads to the conclusion that each carbon dioxide molecule is associated with about 1,000 molecules of chlorophyll. Other experiments on the speed of the 'dark' reaction at high continuous light intensities indicate that one carbon dioxide molecule is reduced when four quanta are absorbed per 1,000 chlorophyll molecules. Again, in the region of low light intensities, oxygen is immediately evolved on illumination. This would not be so if *each* chlorophyll molecule had to absorb the four quanta required. All these results are harmonized if it is assumed that the chlorophyll is absorbed on the surface of the chloroplasts in such a way that about 1,000 molecules are 'energetically' connected, so that a quantum absorbed at any point is transferred without loss to the point where a carbon dioxide molecule is attached. The chlorophyll appears to exist in or on the chloroplasts not in the molecular form, but as some associated complex, perhaps differing from the colloidal form by a greater degree of orientation. This is in harmony with the peculiar difficulties of extracting chlorophyll from leaves with solvents.

The above remarks are sufficient to indicate that it is not surprising that the mechanism of photosynthesis is obscure. It is still uncertain whether the CO_2 is taken up by the chlorophyll or by other cell constituents, whether the oxygen liberated comes from a chlorophyll or a cell-constituent peroxide, whether the presumed transient oxidation products of chlorophyll have lost one or two atoms of hydrogen or have

gained oxygen, and which stages are photochemical and which enzymatic. There is no doubt that the enzyme processes play a large part and that photosynthesis is linked to its apparent opposite respiration, since narcotics, etc., which affect one also affect the other. The use of isotopic elements as 'tracers' has proved a valuable means of advance. When carbon dioxide containing radioactive carbon is used, it can be shown that it is taken up by the plant (*chlorella*) in the dark to give chiefly —COOH groups. This dark reaction may be a primary step in photosynthesis. After exposure to light water-soluble compounds containing —OH and —COOH groups are detectable. By the use of the hydrogen isotopes ^2H and ^3H it might be possible to elucidate the oxidation-reduction processes of the chlorophyll molecule in the plant, but no conclusive results have yet been reached. Finally, by the use of isotopic oxygen ^{18}O experiments show that the oxygen liberated by light comes from the water in the system and not directly from the CO_2 absorbed. When these facts and others are fitted together, the following scheme emerges. The chlorophyll molecules are supposed adsorbed on the chloroplast in groups of about 1,000, i.e. in 'photosynthetic units'. We may imagine either that the coupling is 'optical', i.e. that successive quanta absorbed on different molecules within the unit can move to converge to one locus where a CO_2 molecule is adsorbed, or that it is 'chemical', which requires that adsorbed molecules be free to move over a surface to react thermally or photochemically at particular sites. The CO_2 is probably taken up by a non-photochemical reaction with a cell constituent:



R—H may be a tannin derivative (polyhydroxy phenol) in view of the ease with which these substances react as above. Four successive light quanta, absorbed by chlorophyll, are supposed to bring their photochemical effects ultimately

to bear on the molecule $R\text{---COOH}$, converting it to $R\text{---CH}_2\text{OH} + \text{O}_2$; at least one and probably more temperature-sensitive thermal reactions being also involved ('Blackman reaction'). The $R\text{---CH}_2\text{OH}$ molecule may be then assumed to take up another CO_2 and to undergo a similar set of reactions until finally a sugar molecule is split off regenerating $R\text{---H}$. In the photochemical stages the chlorophyll may either supply H atoms or electrons, but the details of this and of the enzymatic thermal reactions are likely to remain obscure for some time to come.

VIII

THE PHOTOGRAPHIC PROCESS

THE photographic plate consists of a layer of small grains of silver bromide embedded in gelatine and spread on glass or film. Its sensitivity to light is brought to a high value by various manufacturing processes, of which 'ripening', or warming the bromide-gelatine emulsion for some time, plays a large part.

When exposed appropriately to light an invisible 'latent image' is produced. The completion of the photographic 'negative' is carried out by 'development', or treatment with a mild reducing agent, and 'fixing' or removal of unchanged silver halide by a solution of sodium thiosulphate. The development causes the reduction of a certain fraction of the grains to metallic silver. The grains are either completely reduced or unaffected in a proportion dependent on the amount of the exposure.

The nature of the latent image appears to be silver in a very finely divided form. Over-exposure of a photographic emulsion to light results in the formation of visible coloured images, which ultimately become black. These have been identified with silver in the colloidal (cf. Carey Lea's coloured colloidal solution of silver) and fine powder states. Experiments on the rate of loss of halogen by illuminated silver bromide, made with a microbalance, show no breaks indicating the formation of intermediate compounds. X-ray examination also indicates the production of metallic silver.

Quantitative estimations of the amounts of free silver formed in light of known intensity has enabled the quantum efficiency of latent image formation to be obtained. The results approximate to unity for sensitive photographic emulsions, and to much lower values for pure crystals of silver bromide. Evidently the gelatine removes some of the free

bromine atoms produced and prevents a back reaction. It has been estimated that the development process magnifies the amount of silver produced photochemically by a fraction of about 10^5 .

The *blackening* of an exposed and developed plate is not

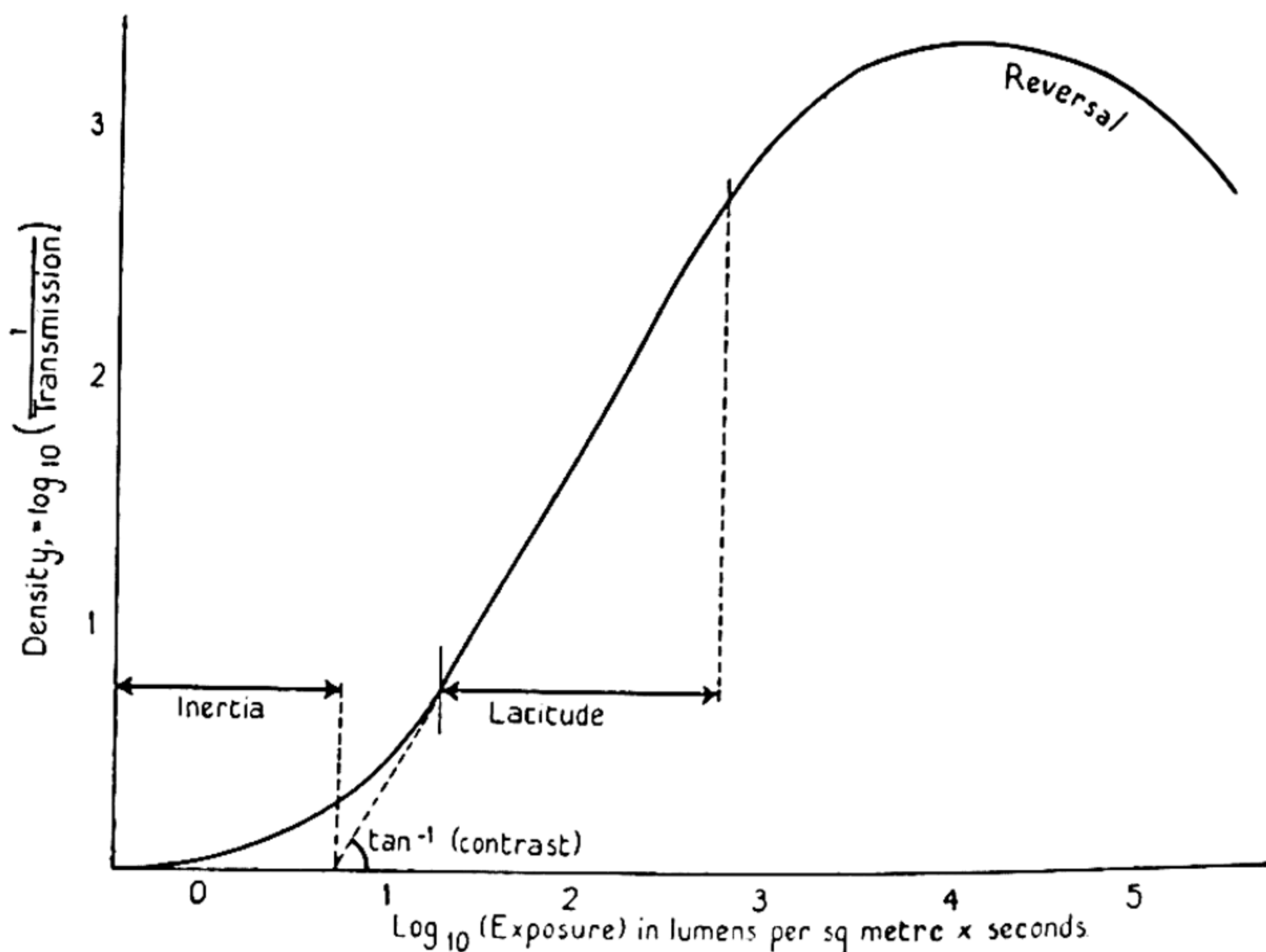


FIG. 48

linearly proportional to the light received. It is measured by finding the reduction in intensity the blackened plate produces when placed across a beam of white light, and is expressed by the 'density' (D), i.e.

$$\log_{10} \frac{\text{light incident on plate}}{\text{light transmitted by plate}}.$$

The general type of relation between the density and the (logarithm of the) light which originally fell on the plate is shown in Fig. 48. There is a straight portion to the curve where uniform contrast is obtained for images formed by lights of different intensities—a range giving the 'latitude' (ratio of amounts of light at two ends of the straight portion) of the plate. This portion may be expressed by the equation

$D = \gamma \log_{10} It^p - i$. The slope of the line, γ , gives the 'contrast', and rises from low values at very short wave-lengths to a constant value of about 1 from 2,500–3,200 Å, increasing in the visible region to values of about 1.4 for fast films to 3.2 for lantern slide plates. i is the intercept on the horizontal axis, and is called the *inertia* (expressed in lumen-seconds per sq. metre). Its reciprocal multiplied by 34 is called the Hurter and Driffeld *speed* of the plate. The Schwartzschild constant p expresses the fact that a plate does not obey the 'reciprocity law', i.e. halving the light intensity and doubling the exposure time does not produce as much blackening as before. p under ordinary conditions is about 0.86. A photographic plate at very low light intensities needs inordinately long exposures, a fact which limits its use when faint lights are concerned, as in astronomy. All the above 'constants', and particularly γ , vary with the wave-length of the light employed. Consequently, if two beams of different wave-length produce equally dense images on a plate in a given time, doubling the intensities of both will result in densities no longer equal. For accurate photometric purposes, therefore, only lights of the same wave-length must be compared by their blackening effects; the exposure times must be equal, and the stronger light cut down quantitatively in intensity by a device of known transmission so as to produce *equality of density* of two neighbouring images on the *same* plate. Since the density depends somewhat on the conditions of development, these must be carefully controlled to secure regularity over the plate area.

The ordinary photographic plate is sensitive to visible light only at the shorter wave-length region of the spectrum, while the eye reacts most strongly to yellow, so that colour contrasts reproduced in monochrome on a plate are incorrect; for example, a dish of light-yellow bananas and dark-blue grapes may appear reversed in appearance of brightness. It has been found that certain dyes, adsorbed

to the extent of about a unimolecular layer (or even less for infra-red sensitizing) on the silver bromide grains, extend the sensitivity to longer wave-lengths (see Fig. 49). Orthochromatic plates approximate in wave-length sensitivity to that

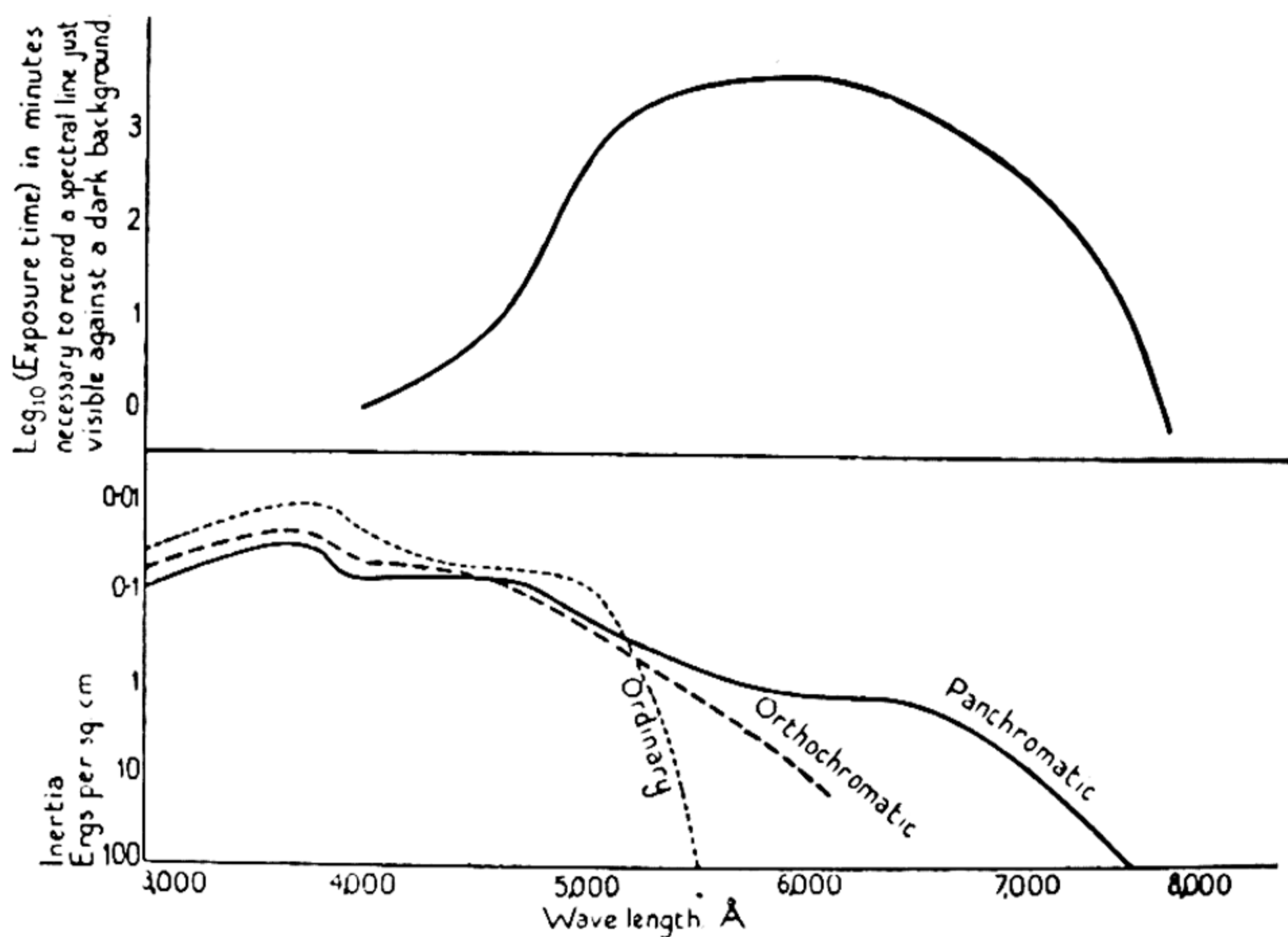
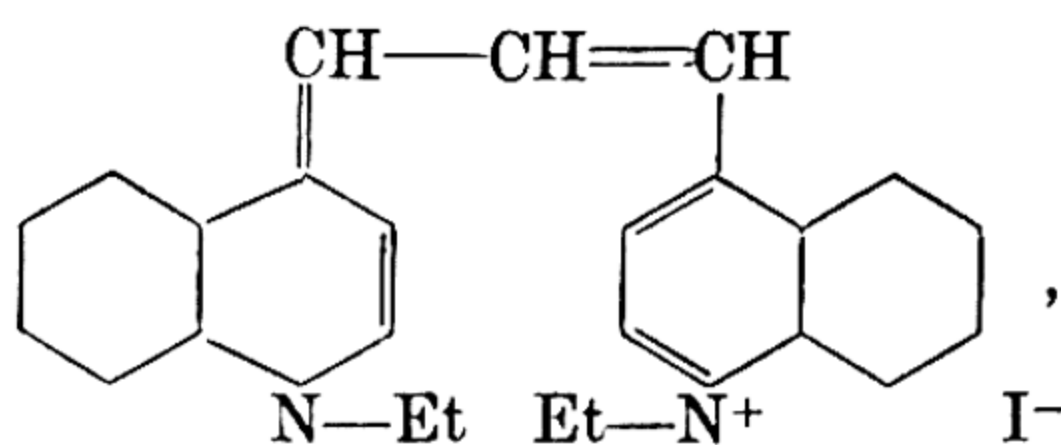


FIG. 49

of the eye. The carbocyanine dyes are particularly effective in conferring red and infra-red sensitivity. Krypto-cyanine,



sensitizes plates to 8,000 Å (panchromatic plates), and xeno-cyanine (1:1' diethyl-4:4' tricarbo-cyanine iodide), having 7 instead of 3 —CH groups (united by odd and even double bonds) between the ring systems, to 12,000 Å. Tetra- and penta-carbo-cyanines are effective to 13,600 Å. Such ultra-sensitive plates do not keep long at the ordinary temperature; they fog through the effect of quanta of 'temperature

radiation in the short infra-red. They are of great use for spectral photography down to the above limits, particularly for the examination of (overtone) infra-red absorption spectra of molecules, enabling the high resolution of ordinary spectroscopy to replace the insensitive methods (using a thermopile) of infra-red work. In conjunction with a red or infra-red filter, they are used for long-distance photography, taking advantage of the smaller atmospheric scattering at long wave-lengths.

It has been shown that sensitizing dyes must have a *planar* structure, i.e. must have a highly conjugated arrangement of π orbitals which impose planarity on the molecule, and that they are adsorbed at a fixed orientation on the 111 planes of the AgBr lattice. It is possible that two types of dye sensitizing may be distinguished, *molecular* sensitizing by the absorption of x and y bands (p. 140) of the dye in the molecular adsorbed form, or *aggregate* sensitizing by the z bands of dye molecules stacked like piles of coins into a 'polymer' (p. 141).

In the short-wave region, beyond about 2,400 Å, photographic plates become insensitive owing to the absorption of light by the gelatine. For use at shorter wave-lengths the gelatine may be largely eliminated by special processes, or an ordinary plate treated with certain oils, or a 1 per cent. solution of sodium salicylate in strong alcohol. The latter substances fluoresce in the short-wave light and the longer-wave emission is taken up by the plate.

When a latent image is formed on a plate, and partly developed, it is found that development begins at certain centres only on the grains. These are not to be explained as points where single quanta impinge. The average grain must absorb about 100 quanta to become developable, and almost as many silver atoms are produced in it, yet it may show only one or a few development centres. Something is present on the grain to which the photochemical products can migrate to build up a nucleus of metallic silver containing a number of atoms.

It had long been known that certain brands of gelatine produced very sensitive emulsions, while others were of little use. By a careful examination of the residues from the processes of the manufacture of the different gelatines it was found that the substances which made some gelatines produce very sensitive plates were sulphur compounds, particularly thiocarbimides. With this knowledge it is possible to activate poor gelatines and make them suitable for producing sensitive emulsions. One part in a million of allyl thiocarbimide is enough to render an inert gelatine active. Thiocarbamides and certain organic substances containing selenium and tellurium instead of sulphur are also effective. These substances in the gelatine probably break down in the process of manufacture of the plate and form minute quantities of silver sulphide (etc.), which is adsorbed on the bromide grains to produce the sensitive centres.

An interpretation of the primary processes occurring when light acts on a plate has been given by Mott. The photographic plate consists of an emulsion of silver bromide, on the grains of which may be minute specks of silver produced by the 'ripening' process, and of silver sulphide from sulphur compounds present. Silver bromide has an ionic lattice and shows photoconductivity, i.e. mobile electrons are liberated from the bromine ions in the lattice (possibly largely from those near cracks, since the absorption is at the tail end of the band). These mobile electrons, moving in the 'conduction' band of the crystal (p. 149), are *trapped* by the specks of silver or of silver sulphide, which offer unoccupied energy levels to the electrons lower than those of the ionic lattice. The specks therefore accumulate a high negative charge. In addition to this *electronic* process, *ionic* conductivity is present. At the ordinary temperature silver bromide conducts an electric current *electrolytically*; the effect is ascribed to the imperfections in the lattice whereby some silver ions are displaced, by thermal processes, into inter-

lattice positions. Such interlattice silver atoms are mobile, even at the ordinary temperature, and they move towards the charged speck and there discharge themselves as a process of electrolysis. The movement is of two kinds, direct movement of the ions from one interstitial position to another, and the filling up of the vacated sites by silver ions in the lattice, producing new vacant sites, so that the 'positive holes' (p. 149) migrate. A silver nucleus is thereby built up at one or more points at the surface of the crystal grain. The bromine atoms formed by the light 'diffuse' to the surface, not directly, but by exchange of charge between successive bromine ions in the lattice, and are removed by the gelatine of the plate. When the silver nuclei contain about 200 atoms they have reached the average size of a nucleus of the 'latent image', and are capable of 'development'. Development is merely a continuation of the process of electrolysis. The developer ion supplies electrons to the silver nucleus, charging it negatively, and causing the discharge of more silver ions, until ultimately all the silver is deposited on the original nuclei. The shape of the resulting silver is often a long coiled filament due to mode of formation as an electrolytic growth, resembling the 'Pharaoh's serpents' of ash from ignited mercuric thiocyanate. These processes are shown in Fig. 50.

Using the hypothesis described above, it is possible to account for the failure of the photographic plate to obey the 'reciprocity law' over all ranges. At very low light intensities the rate of arrival of electrons at the 'sensitivity specks' is extremely slow, and insufficient to overwhelm the possibility of the loss of electrons by thermionic emission back to the lattice. At high light intensities a large number of mobile electrons are produced, but each 'sensitivity speck' cannot take more than one at a time, owing to its small electrical capacity and the high voltage resulting from electron trapping. While the slow-moving silver ions are migrating

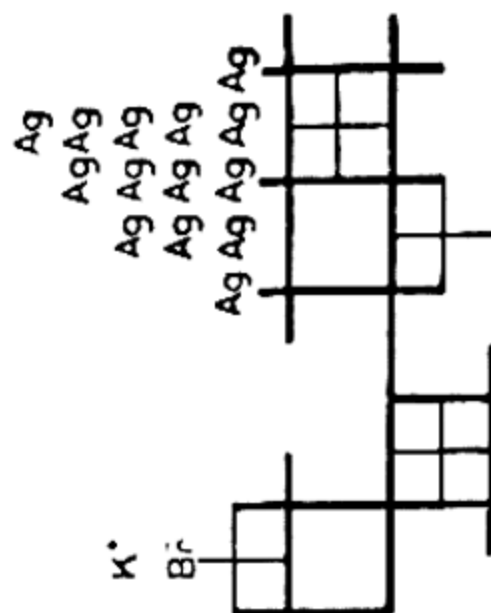
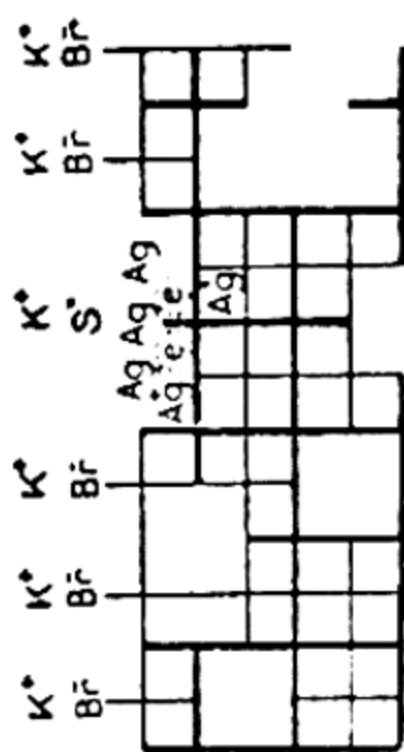
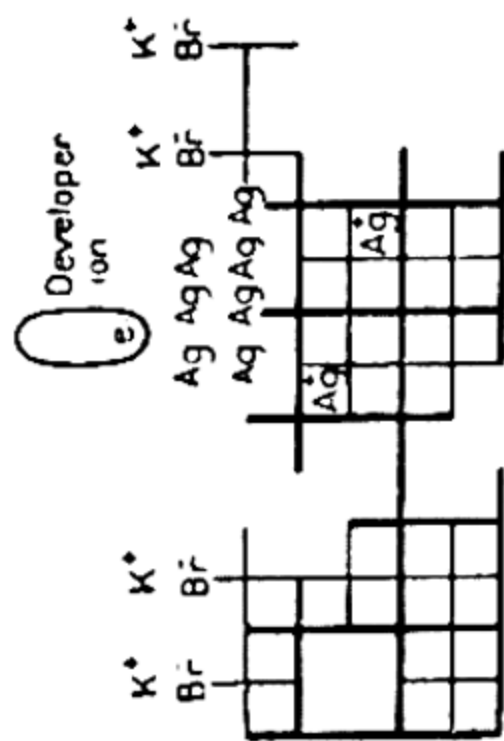
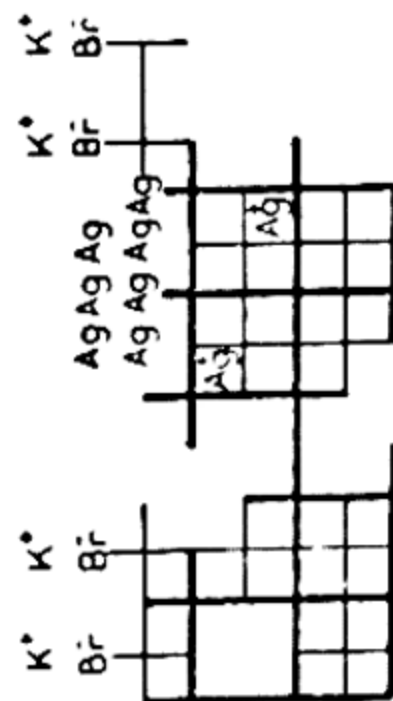
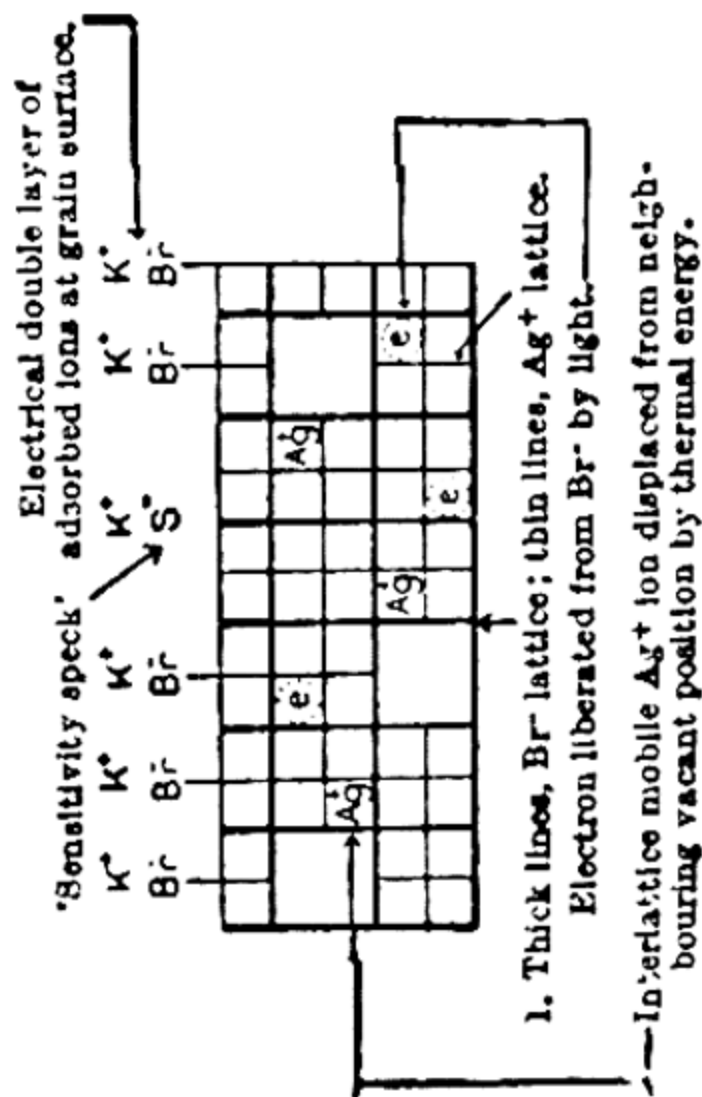


Fig. 50. The Photographic process.
1-4 exposure: 5-6 development.

to the 'specks' there is a 'waiting list' or concentration of electrons accumulating in the grain which attack weak points in the lattice to give silver nuclei in the interior. These are largely wasted in the ultimate development process, though different developers, depending on their capacities to dissolve silver bromide, may utilize them to varying extents. At some intermediate light intensity the 'reciprocity law' may be approximately correct. With very short exposures at extremely high light intensities the 'law' is again valid, since the exposure time is short compared with the movement of the ions, and the light has ceased to act before they have migrated to the 'sensitivity specks'. These processes are temperature sensitive. At low temperatures the ionic conduction will cease; interlattice silver ions will be 'frozen in'. The thermionic emission is also checked at low temperatures, so that electrons, which remain mobile, can accumulate without loss in the 'traps'. On warming up to normal temperature the interlattice ions are freed and migrate to the traps. Under these conditions the reciprocity law should be obeyed, and experimental evidence has been obtained that it is. There is a reduction in overall sensitivity of the plate at very low temperatures, however, which awaits interpretation. It may be due to a reduction in the quantum efficiency of the primary process, to a change in the fraction of the light absorbed, or to other reasons.

The Herschel effect (diminution of developable density of a latent image by exposure to red light), on these views, is interpreted as the photoelectric ejection of an electron by red light from a charged 'trap' back into the 'conductance band' of the lattice, forming a silver ion which migrates away from the sensitivity speck. The action of photosensitizing dyes appears as follows. The dye-stuff molecule, adsorbed on the grain, absorbs a quantum and becomes an excited molecule with an electron displaced to an outer orbital. An electron from the lattice may enter the vacated

dye orbital giving a radical dye ion. The negative charge may pass over the surface by a process of exchange between neighbouring dye molecules and ultimately reach a sensitivity speck.

The 'reversal' or solarization effect, where the developable density of a plate is reduced when it has been exposed to very strong light intensities, has been shown to be due to the encrusting of the silver nuclei by silver bromide formed when the rate of production of bromine atoms by light is too great for them to be quickly removed by the gelatine present; this coating effect slows up development unless the solution can dissolve the silver halide. Many other of the complexities in the behaviour of the photographic plate can be interpreted more or less clearly along the above lines. The Clayden effect, namely the desensitizing of a plate by brief exposure to high-intensity light, may be ascribed to the formation of internal silver nuclei which later (on subsequent exposure) compete for photo-electrons with the 'sensitivity specks' on the surface. Explanations may also be found for other effects arising from the pre- or post-exposure to high or low intensities of plates which have been underexposed to light of high or low intensity. The function of the processes of manufacture may also be understood. The 'ripening' process increases grain size, and large grains are more sensitive because they present a larger target area to the light and have more interstitial ions to feed the latent image speck. 'Digestion', or the further heating of emulsion after the 'ripening' process, surplus bromide now being removed, allows the 'sensitivity specks' to form; the optimum time of 'digestion' is passed when several specks are formed on each grain, since these reduce efficiency by their mutual competition during exposure. Too long 'digestion' also leads to 'fogging' through the formation of silver nuclei capable of development without exposure.

IX

THE REACTIONS OF THE EYE TO LIGHT

THE human eye consists essentially of a *lens*, capable of some adjustment of focal length, and a *retina*, or light-sensitive screen, upon which light images are produced. Two light-sensitive elements are recognizable when the retina is examined with a microscope, the *rod* and the *cone* cells, and these are connected to nerve-fibres in an exceedingly complex way, the fibres ultimately passing into the optic nerve of the eye. The eye has the power of adapting itself to function satisfactorily over an enormous range of light intensity, at least 10^6 to 1, partly by the contractile *iris* but mostly by the equilibrium between strong light bleaching away the light-sensitive material and the steady production of fresh material by the retina. These chemical processes are slow, so that complete adaptation takes time; about 20 minutes in the dark is necessary for full sensitivity to be built up. Because of adaptation the eye has little power of judging *absolute* light intensities but can only estimate *relative* intensities. For light of moderate intensities the least perceptible increase in intensity ΔI is a definite fraction of the intensity I , $\Delta I/I = 0.016$ (Weber-Fechner law), i.e. intensities must differ by more than 1.6 per cent. to be distinguished. This sets a limit to the accuracy of optical measurements. At very low intensities the ratio rises to 0.5 or higher. The best intensity of brightness for contrast (in photometers, etc.) is 8–20 millilamberts, while for reading purposes about 30 millilamberts, or 1,000 lux, is most satisfactory.

The rods and the cones, which appear to be the primary receptors of the light reaching the retina, have different functions and are differently distributed. Clear vision, at moderate to high light intensities, occurs only when the image is focused on the *fovea*, the centre of the *yellow spot*,

which contains a high proportion of cones. The cones are also the agents which distinguish *colour*. Away from the yellow spot vision occurs through the action of the rods, which are not capable of distinguishing colours but are more sensitive to feeble light. Faint light is then best seen when the image is focused away from the fovea. The retina contains about 3×10^6 cones and 18×10^6 rods, whose diameters are only 3 or 4 wave-lengths of light.

It is possible to compare with a photometer the relative *luminosities* or brightnesses of differently coloured lights with one another. By the use of monochromatic lights and a 'flicker' photometer the 'equal energy luminosity' curves of Fig. 51 are obtained. These represent the reciprocal of the energy at each wave-length region necessary to give a constant visual sensation. Two curves are shown, one for high and the other for low light intensities, measured for light arriving at the eye (ocular). Owing to light absorption in the refractive media of the eye the shorter wave-lengths are reduced in intensity when they reach the retina, which is therefore more sensitive to these radiations than the ocular visibility curve suggests. The true retinal sensitivity curve for scotopic vision, corrected for this effect, is shown in the figure in addition to the simple ocular curve. The figure shows that the point of maximum sensitivity of the eye is different for rod (scotopic, low intensity) and cone (photopic, high intensity) vision. If two colours, say red and blue, are matched in luminosity at moderately high light intensities, and both are reduced in equal proportion, the blue will appear brighter than the red as rod vision replaces that of the cones—the Purkinje effect. The relative luminosities will also depend on the particular part of the retina on which the images are focused. At brightnesses in the neighbourhood of 0.25 millilambert, (or 0.2 equivalent foot-candles), the visibility curve lies about half-way between the two curves of Fig. 51.

From the retinal rods of the higher animals (most conveniently from frogs) a coloured substance may be isolated in some degree of purity known as the *visual purple*. Its solutions are photochemically bleached by light with a quantum efficiency of about unity, and the plot of its extinction

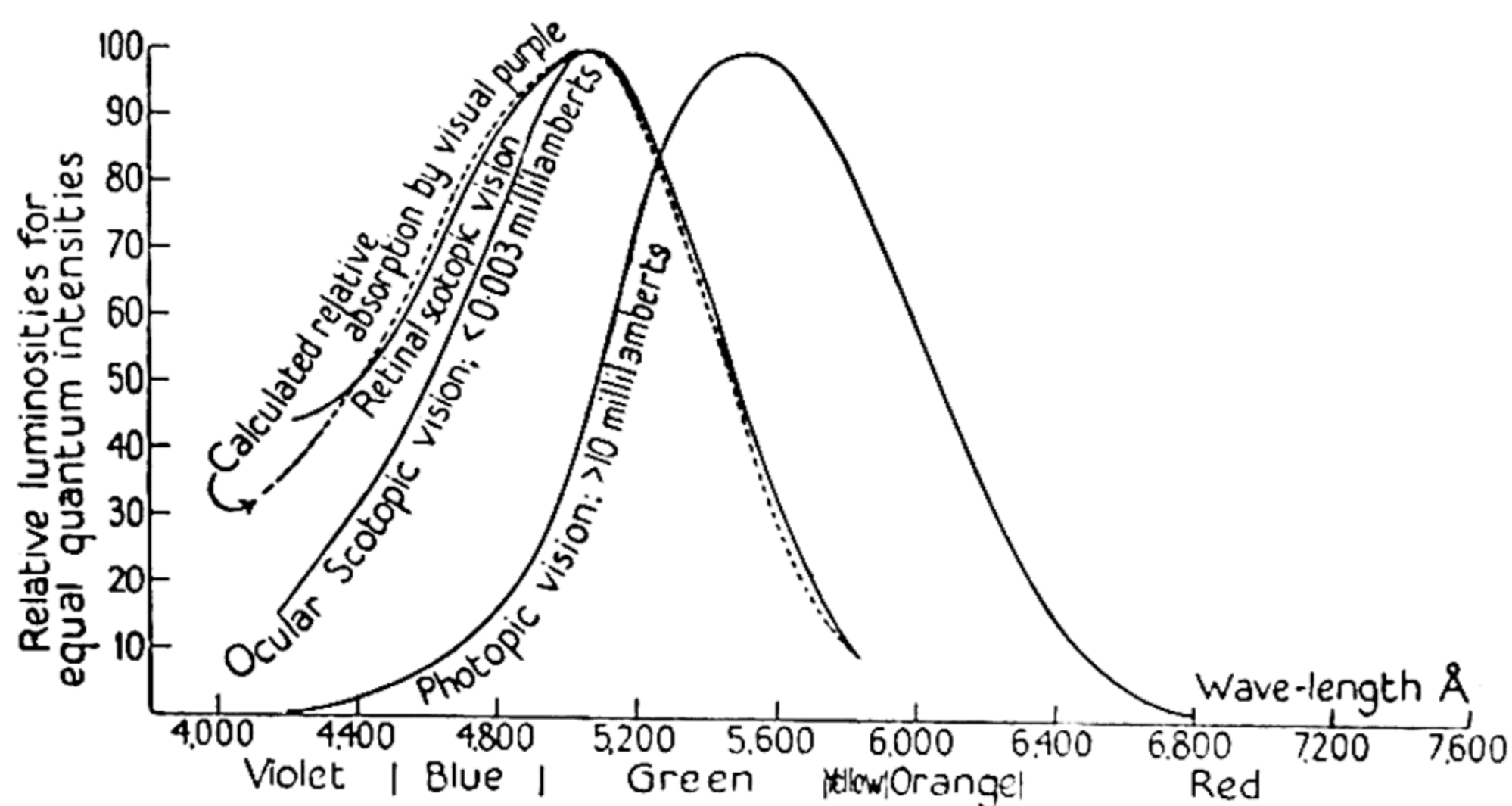


FIG. 51

coefficients against wave-lengths has a spectral distribution very close to the *retinal* scotopic luminosity curve (see Fig. 51). This corresponds to the light absorbed if the absorption by the rods is small. Scotopic vision may then be ascribed to a photochemical change of the visual purple on the rods of the retina. The chemical nature of visual purple is a protein to which is attached carotenoid substances—bodies containing a chain of twenty-two carbon atoms united by alternate single and double bonds and related to vitamin A. A deficiency of the latter substance has been shown to produce 'night-blindness'. Its absorption in the visible region arises from its highly conjugated nature (see Fig. 32).

The problem of photopic vision and colour perception is more complex. At higher light intensities the visual purple on the rods is largely bleached and the cones take over. The adjustment of the eye to different light intensities is accom-

panied by a balancing of the rate of destruction of the photo-active material with its regeneration in the eye, rates which are different for the rods and the cones. The following well-marked colours are observed by a normal eye in the spectrum of white light:

<i>Wave-length Å</i>	<i>Colour</i>	<i>Complementary colour (= white—colour)</i>
7,500–6,050	Red	Blue-green
6,050–5,950	Orange	Green-blue
5,950–5,800	Yellow	Blue
5,800–5,600	Yellow-green	Violet
5,600–5,000	Green	Purple
5,000–4,900	Blue-green	Red
4,900–4,800	Green-blue	Orange
4,800–4,350	Blue	Yellow
4,350–4,000	Violet	Yellow-green

Between 4,000 and 3,135 Å ultra-violet light produces a fluorescence of the retina, and at shorter wave-lengths conjunctivitis is caused. About 150 different *hues* can be distinguished in the spectrum, and about 20 other purple hues can be made by mixing reds and blue-violets. About two million distinct *colours* may be produced from these hues by viewing them mixed with different amounts of white light and at different total intensities. A *colour sensation* is characterized by its *brightness*, its *unsaturation*, or *tint*, namely, the extent to which it is diluted by white, and its *hue*, which is its colour value apart from the first two quantities. The sensation of 'white' (absence of hue) arises when the eye receives all the spectral hues together in the proportion they occur in 'white light', e.g. sunlight. A white sensation is also produced by a great number of other physically distinct combinations of hues if mixed in appropriate amounts. For example, monochromatic red (6,300 Å), green (5,280 Å), and blue (4,570 Å) may be blended to a white, as may the union of pairs of monochromatic hues (complementary hues), e.g. 6,090 Å + 4,940 Å mixed at equal brightness, 5,760 Å +

4,750 Å at a 10 : 1 brightness ratio, or yellow + violet in 100 : 1 ratio. It is further found that every known hue may be matched by appropriate mixtures of three hues, one red, one green, and one blue. A number of sets of monochromatic hues serve for this purpose, or even reds, greens, and blues consisting of broad spectral bands as produced by light filters. The hue of yellow light, of wave-length 5,890 Å, for example, is counterfeited to the eye by a mixture of red (6,708 Å) and green (5,350 Å). The mixing may be either direct, or by rapidly alternating one hue with the other, or by directing one hue into the right eye and the other into the left. The *exact colour* is not reproduced, since the mixture contains more white than the spectral yellow, i.e. is lighter in tint or less *saturated*, but if white is added to the spectral yellow, a perfect *colour* match is achieved.

Colour-mixing of this kind is called *additive* and refers to the actual mixing of different colours as by simultaneously illuminating a white surface with them. Examples are the light emitted from a gas-discharge tube, as a mercury lamp, where the monochromatic radiations combine to give a very pale colour tending towards white, and the mixing of differently coloured phosphors together to produce a 'white' cathode-ray tube fluorescent screen.

When white light is passed through a succession of coloured screens, each of which *removes* a spectral region, the tendency is towards black, instead of white as above, when the number of components is increased. This is referred to as a *subtractive* effect. Subtractive effects occur when paints or pigments are mixed; e.g. a mixture of yellow paint, which reflects only yellow and green in white light, and blue paint, reflecting only green and blue, appears green since this is the common unabsorbed constituent. Hues and colours may be simulated by subtractive effects. The necessary colours (conventionally called 'primaries') are cyan (white less red), magenta (white less green), and yellow (white less blue).

Screens of these colours, of variable depths of tint, through which a beam of white light successively passes, can be utilized to match any selected coloured object. All processes of colour photography and of colour printing utilize the principles either of the *additive* or the *subtractive* effects of colour production. Their fidelity is of course affected by the limitations of the coloured materials available, which may not have the necessary light-absorbing properties to provide a perfectly balanced three-colour system.

Owing to its very subjective nature colour is not easily and satisfactorily expressible by physical quantities. The most fundamental method of measuring the light emitting, absorbing, or reflecting powers of a body is that of spectrophotometry (p. 55), whereby a curve is obtained giving the amount of light of every wave-length. Such a curve, however, is not readily interpreted in terms of the sensation of colour. For example, a substance which absorbs the green, blue, and violet spectral ranges only from white light will appear yellow, but similar yellows will result from totally different absorption curves, as a curve showing transmission or reflection in a narrow region near $5,900 \text{ \AA}$, or in two narrow regions in the red and green parts of the spectrum. Further, a yellow colour, if viewed in the same light at reduced intensity, changes to a brown. Though it is possible to interpret the colour of any given spectral distribution of light by suitable analysis the answer is not immediately obvious from the measurements, so that other methods of colour specification have been sought. Colorimeters have been devised to measure colour by determining the relative amounts of three suitably chosen radiations necessary to match it. The colour to be measured is viewed in one half of a divided eye-piece field, while the other half is illuminated by the three coloured lights whose intensities can be varied. The principles of either *additive* mixing of red, green, and blue lights, or the *subtractive* effect of white light passing cyan,

magenta, and yellow filters may be used. As it is arranged that the two halves of the field are matched for colour at practically equal intensities, and light intensity is not to be included in the colour measurement, we have only three variables, and:

$$\text{colour} = aR + bG + cB,$$

where a , b , and c are the experimentally determined amounts of the three chosen standards R , G , and B , required for matching, and $a + b + c$ can be arbitrarily equated to unity. Two coefficients only, say a and b , are then required to specify the colour.

When this kind of measurement is carried out in practice it is found that certain colours have *negative* coefficients, which means that to match the colour with the three standards some white (given by $a = b = c = 0.333$) must first be added to it. This, together with the latitude allowable in choosing the standards, has made it desirable to modify the nature of the specification in terms of coefficients. By international agreement the measured coefficients obtained on any particular instrument are subjected to a linear transformation to another set of coordinates,

$$\text{colour} = xX + yY + zZ,$$

X , Y , and Z no longer being 'real' colours but coordinates which are precisely defined by the x , y , and z values assigned by agreement to red light at 7,000 Å and to the blue and green mercury lines. The white-point, $x = y = z = 0.333$, is the point on the graphical representation corresponding to white light composed of all the spectral hues, every narrow wavelength interval having equal energy. Since $x + y + z$ is set equal to 1, a two-dimensional graph of x and y is sufficient to represent all colours. The specifications of the coordinates were ingeniously so chosen that the y value of a colour also gives its relative 'luminosity' to a white light of equal energy. Fig. 52 shows a plot of the loci of monochromatic

spectral radiations in terms of x and y (C.I.E. diagram). The 'saturated' hues lie round the curve, white is in the centre, and any 'unsaturated' or 'pale' colour may be assigned coordinates somewhere within the enclosed area. The inner curve passing from the red towards the centre, for

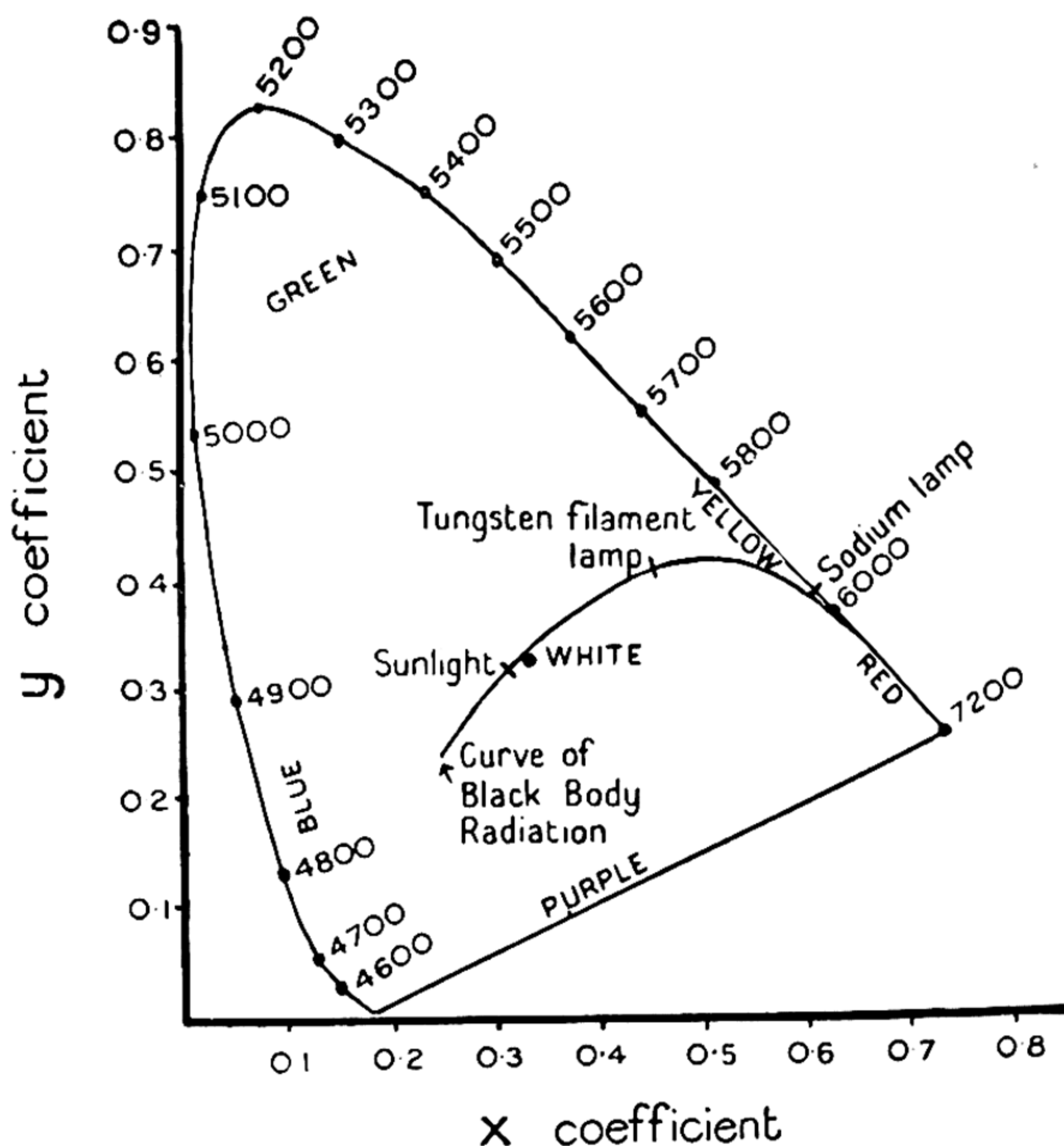


FIG. 52. C.I.E. Colour Diagram 1931.

example, is the locus of the colour of the light from incandescent solids, i.e. 'black-body' radiation (temperature increasing from right to left). In this way a precise specification of a coloured light as two coefficients may be made, and also of a coloured substance if the illuminating white light is specified. The measurements of course presuppose that the observer who makes them has a colour vision not too far from the 'normal' (see below). The C.I.E. system has one defect,

namely that visually equal 'steps' of colour difference are represented on the diagram by very unequal distances. Modified plotting systems have been proposed to reduce this defect, but have not been universally adopted. One point is clearly brought out by the diagram when it is remembered that the y coordinate specifies the 'luminosity' of the colour. Greens are highly luminous, violets are necessarily dark. The latter of course reflect or transmit light only from parts of the spectrum where the eye is very insensitive.

An alternative method of specifying a colour represented by any point on Fig. 52 is to draw a line through it and the 'white' point to cut the spectral locus. This intersection gives the 'dominant wave-length' and the ratio of distances along the line of the point and of the intersection from the 'white' point the 'excitation purity' of the colour. If the colour is purple, the line must be prolonged through the 'white' point to give the 'dominant wave-length' of the (approximately) complementary colour.

To give greater 'objectivity' to measurements of this kind colorimeters employing photocells to receive the colours to be compared have been devised. These eliminate the human element of possibilities of abnormal vision, but need very careful setting up if they are not to introduce similar abnormalities of their own.

The most direct determination of colour in closest accord with human sensations and capable of expressing intensity effects is the Munsell Colour system. The five hues, red, yellow, green, blue, and purple, are arranged in segments round a horizontal circle, so that the angular position of a point round the circle defines its hue, and its radial distance from the centre its saturation (called *chroma*), the colours paling to white at the centre. A whole series of such planes of measurement are supposed piled one above the other with a common central axis of which the top is white (100 per cent. reflection or transmission of white light) and the bottom

black. Coordinates along this axis are termed the *value*, measuring the lightness or darkness of the colour. The *hue*, *chroma*, and *value* coordinates of a colour are more readily related to artistic appreciation as in problems of dyeing or decoration than any other specification.

The mechanism by which the eye recognizes colour has long been sought after by investigators. So far no coloured substance has actually been extracted from the cone cells as visual purple has been obtained from the rods, but there is very little of the latter, and the lower sensitivity of the cones is almost certainly due to an extremely low concentration of photoactive material. We may confidently start from the hypotheses of the presence of coloured photoactive substances allied to visual purple on the cone cells, and that each absorbed light quantum destroys a molecule of such coloured receptors.

Since experiment shows that all colours can be matched by mixtures of three suitable standards, it has been commonly assumed that three separate receptors are present on the cones, one responding to red, one to green, and one to blue, and that their relative stimulations gave the sensation of colour. This 'trichromatic' theory was first postulated in 1801 by Thomas Young after experiments which included the detection of the colour blindness of John Dalton. As a working hypothesis it has been largely successful in explaining the facts of colour mixing and colour blindness. It is of course unable to account for many complex phenomena shown by the eye which appear to be due to nerve processes occurring at different levels in the complex nerve network between the cones and the optic nerve or the brain, e.g. the synthesis of composite colours by viewing different colours with the two eyes, and various contrast colour phenomena. Its wide range of usefulness has naturally caused attention to be paid to the possibility of determining the 'spectral sensitivities' of the hypothetical receptors, each of which would

represent the absorption curve of the substance concerned (since the fraction of light absorbed is small), and whose sum should give the luminosity (photopic) curve of Fig. 51. This has proved a most elusive matter. Colour mixing data cannot provide a unique solution. Fig. 53 shows one relevant matter.

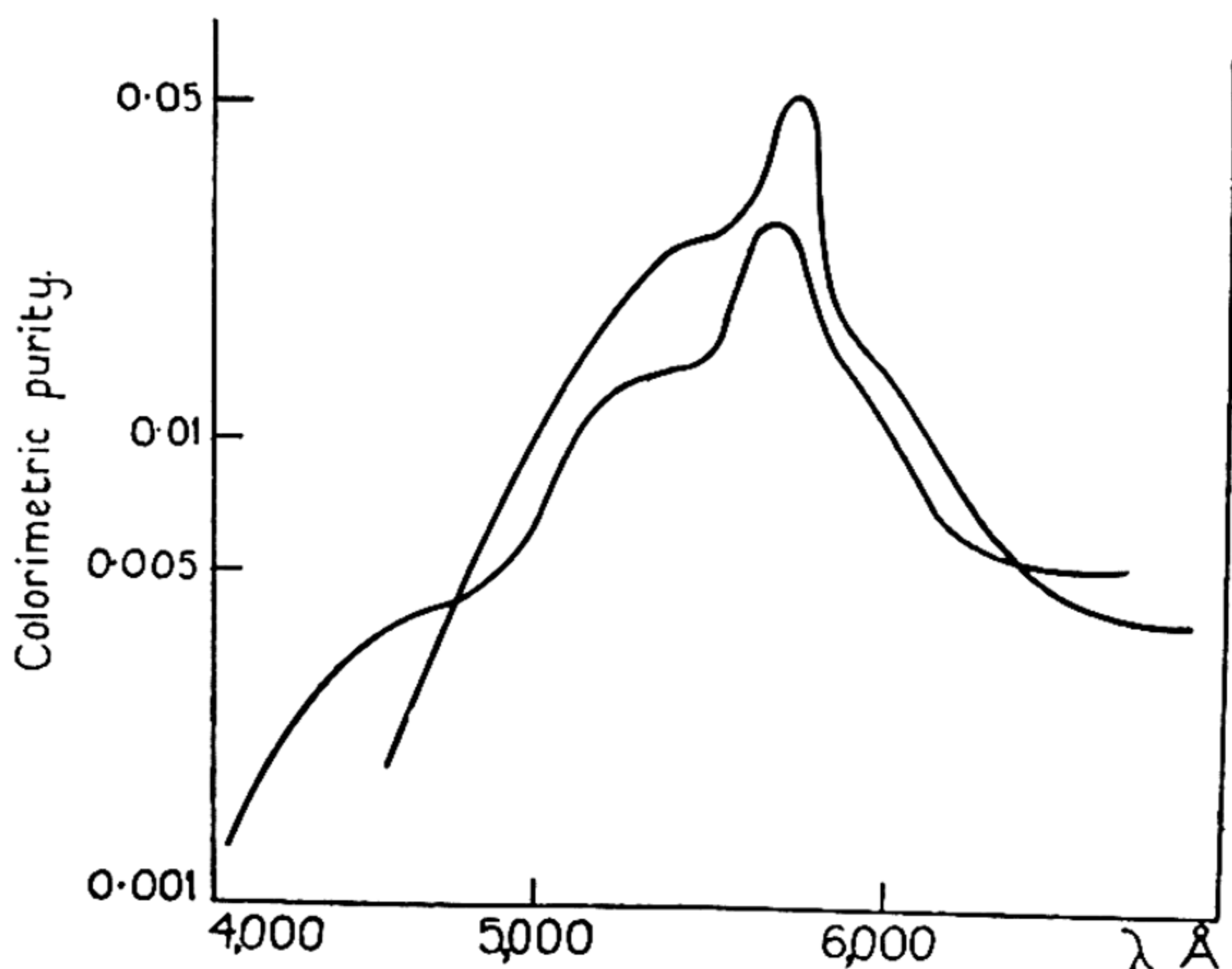


FIG. 53. Curves of unsaturation of spectral colours.
(Results of two observers).

The curves indicate that even the so-called 'saturated' spectral colours are really highly unsaturated, as shown by mixing experiments on white and coloured light. The absorption curves of the colour receptors in the eye must therefore overlap one another considerably, so that even monochromatic radiations stimulate more than one in appreciable degree. The majority of investigators in the past have favoured the assumption of three broad and overlapping bands with maxima at about 5,900, 5,500, and 4,700 Å to represent the colour sensitive receptors, but an infinite number of mathematically equivalent solutions were possible, including some with three bands covering the whole visible

region with maxima in the yellow-green and separated only slightly from one another (Hecht).

By means of a new physiological technique Granit has advanced this problem much nearer its solution. It has proved possible to insert a microelectrode into the retina of an anaesthetized animal and to record electrically the nerve stimulation produced by light. The spectral sensitivity of the nerve fibre reached by the electrode is then determined by finding the threshold energies for response for light of different wave-lengths, the reciprocal of this quantity giving the sensitivity when the energy has been converted into quanta. For dark-adapted eyes a sensitivity curve is obtained practically identical with the human retinal scotopic curve of Fig. 51, which is also identical with the absorption spectrum of visual purple plotted on a quantum basis. Rod vision in man and animals is therefore entirely adequately attributable to the common light-sensitive substance visual purple. A different behaviour is found for light-adapted eyes, where the sensitivity of the eye is reduced and bright light vision comes into play. Here the record of the microelectrode varies from experiment to experiment, depending on the nature of the nerve fibre reached. Sometimes narrow sensitivity curves with a half-width of about 600 Å are obtained, as shown in Fig. 54 for a frog's eye. These must either correspond to or closely approximate to the characteristics of the ultimate receptors of colour. Instead of just three curves being observed, however, as expected on the trichromatic theory, every experiment produces a somewhat different curve, and these group themselves in three preferential regions 6,000–5,800 Å, 5,400–5,000 Å, and 4,700–4,500 Å. Evidently therefore the facts are more complex than the simple theory indicated. Visual purple is a substance whose chromophoric group (long chain of alternate single and double bonds) can exist in a large number of cis-trans forms, as well as having the possibility of different modes of adsorption on the cone

cells. The variable experimental results for wave-length sensitivities probably arise from the effects of these factors on the absorption band. In the above experiments (with light-adaptation) it more often happens that the micro-electrode record gives one single broad band, which in eyes

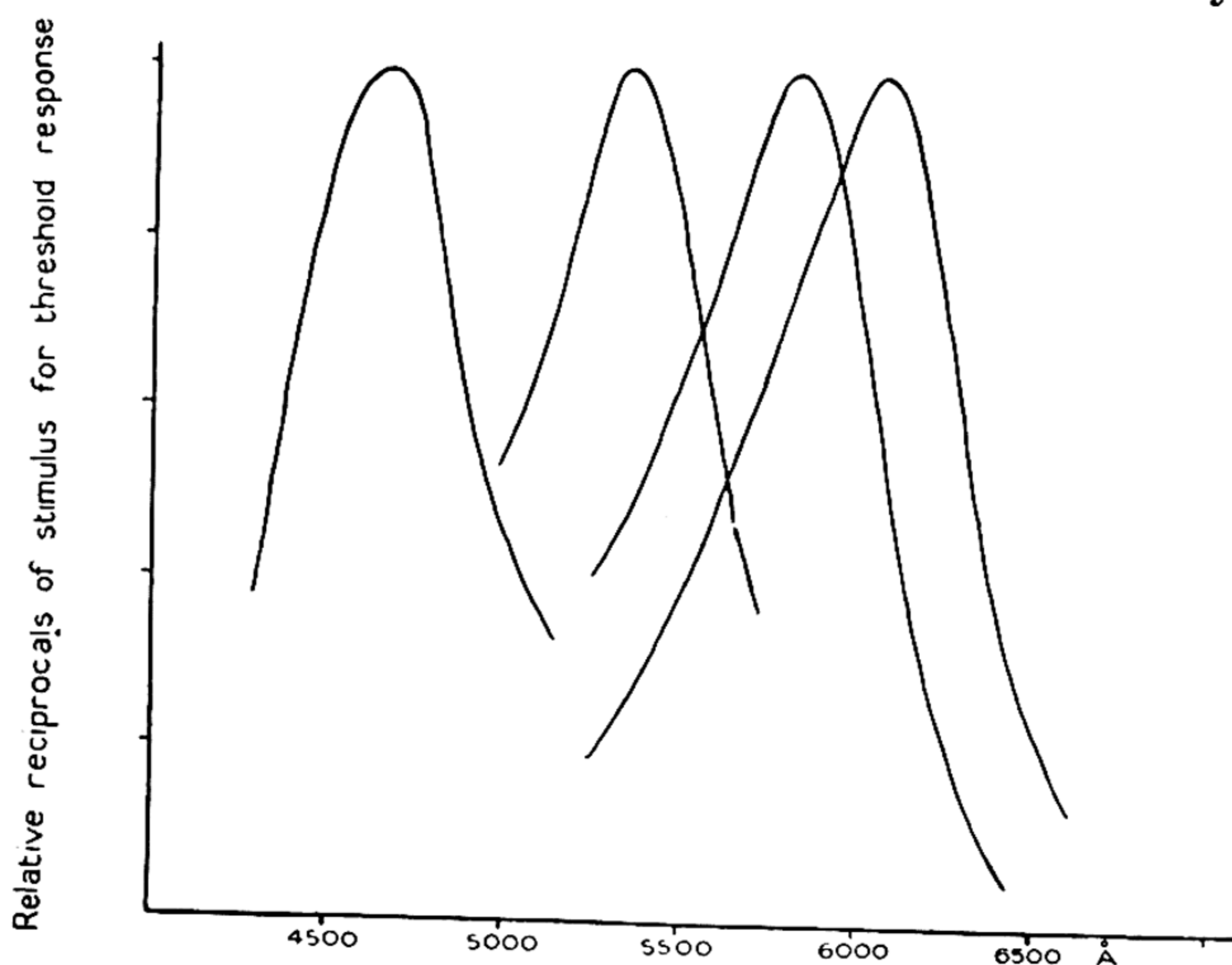


FIG. 54. Sensitivity elements of a light-adapted frog's eye.

having cone cells, as those of the frog or snake, closely resembles the human photopic curve of Fig. 51. For eyes having rods only, as those of the guinea-pig or rat, the single broad band is observed at low intensities only, as with all eyes, and when light-adapted to high intensities the narrow type of bands appear solely. The broad 'photopic' type of band observed in light-adapted eyes equipped with cone cells quite clearly seems to be the summation of the narrower types of curve as shown in Fig. 54. When the microelectrode gives this band, it must have reached either a fibre joined to a cone cell with many kinds of visual purple molecules adsorbed

on it, or a fibre to which are connected as a unit a group of cones whose sensitive elements represent many of the possibilities. Microscopic examination of the human retina shows clear evidence of lateral interconnexion and convergence in the complex structures between the cones or rods and

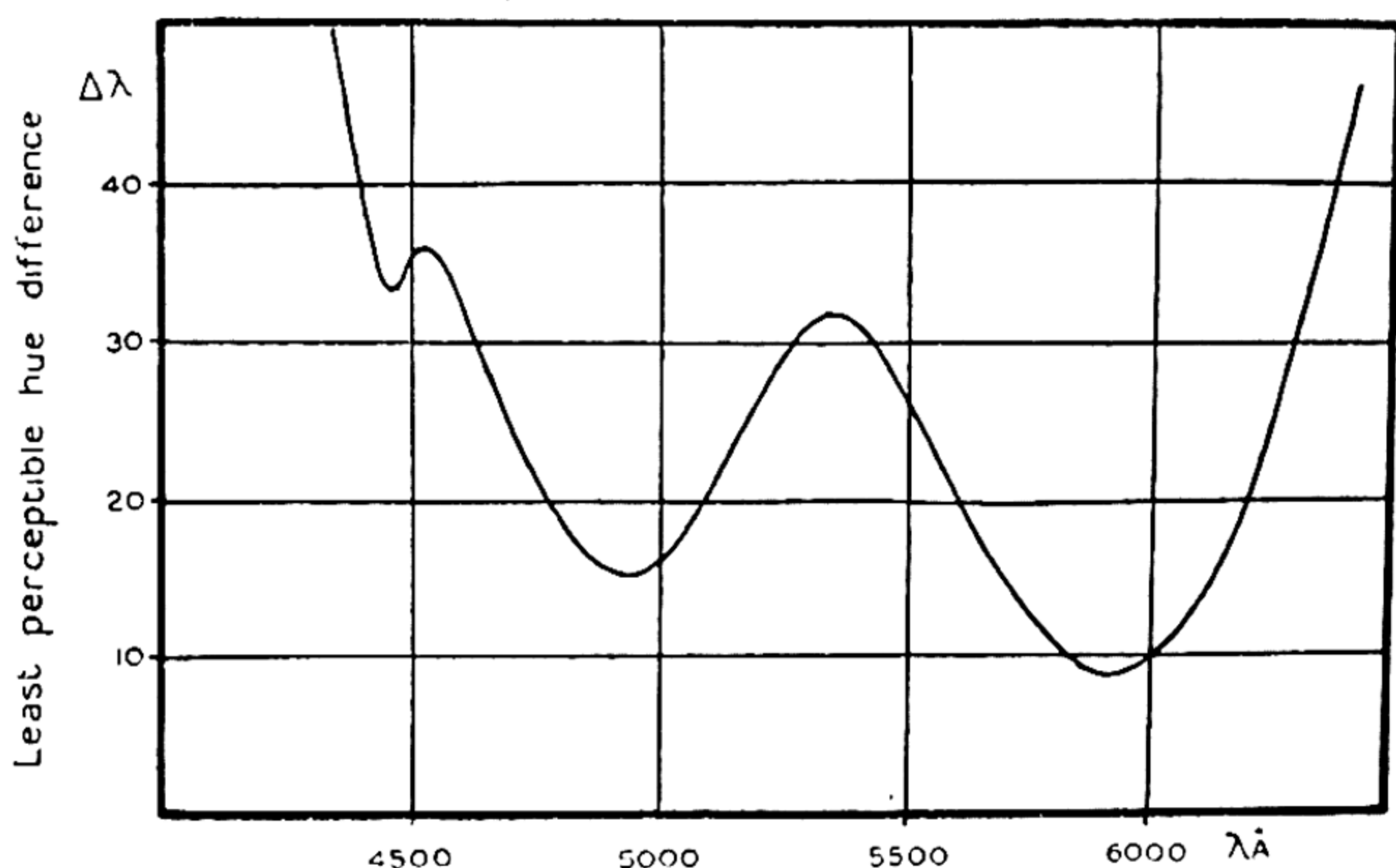


FIG. 55. Hue discrimination curve.

the optic nerve fibres. It is significant that the interconnexion is much less for the cones, where the microelectrode sometimes detects the narrow bands of Fig. 54, than the rods, where only the broad type of band has been observed. The association of the broad band response with coupled receptor cells is therefore probable, and responses from these units give the sensation of white and the measure of the 'luminosity' of colours.

Fig. 55 is a curve showing the power of the light-adapted eye to discriminate between colours. There are three minima, corresponding to wave-lengths where discrimination is easiest. These can be associated with the overlapping regions between the groups of narrow bands of the light-sensitive elements lying in the red-yellow, green, and blue wave-

length ranges, where colour differentiation would be expected to be at its best.

Summarizing these facts and theories we may interpret colour vision thus:—

- (a) Visual purple is a variable substance whose different forms are adsorbed on the cones to give light-sensitive elements of narrow wave-length ranges. The different bands, however, may be grouped into three main regions, red-yellow, green, and blue.
- (b) Groups of light-sensitive elements are interconnected together with a wave-length sensitivity corresponding to the broad band of the photopic curve, and act in unison to convey the sensations of 'white' and of 'luminosity'.
- (c) Lesser groups of elements with bands all in one of the above three main regions act to produce the sensation of colour.

The actual photochemical behaviour of the light-sensitive material is unknown. Visual purple is photochemically bleached in solution, and the loss of sensitivity on light-adaptation is referable to a similar change occurring on the rods. Curves of recovery of sensitivity of the *fovea* after fatigue by bright light show that a simple one-stage photodecomposition and a dark re-formation of sensitive substance are not sufficient; a more complex set of stages must be assumed. The appearance of a complementary colour when a white surface is viewed after fatiguing the eye by a bright coloured light is interpreted as the temporary exhaustion of some of the colour receptors. The *persistence of vision*, which prevents the eye from observing light fluctuations more rapid than 15–20 per second, is almost certainly due to slow chemical changes in the retina and not to nerve or brain processes.

Colour blindness is a matter of fundamental importance in theories of colour vision. A *trichromat*, or person of normal

vision, requires three suitable standard colours to match any selected colour, which he can represent as α Red + β Green + γ Blue, where α , β , and γ are coefficients giving the amounts of the three standards used. The coefficients in any actual case are not identical for different observers. Slight differences exist between the shapes of the photopic curve of Fig. 51 when different subjects are measured, and the curve there shown is a mean one adopted by international convention. These deviations even among trichromats with apparently 'normal' vision may be ascribed to slight relative differences in the number and distribution of the ultimate light-sensitive elements with narrow sensitivity bands within the larger groupings of red, green, and blue types. More abnormal are the *dichromats*, whose colour sense is so reduced that they can match any colour as seen by them by the use of two suitable standards only. There are two chief types of dichromat, *protanopes* and *deutanopes*. The former lack red-sensitivity, and have been known to wear a red tie at a funeral. Deutanopes are called red-green blind, and find it difficult or impossible to detect any change of colour in methyl orange during a titration, or to find red objects left lying in the grass. Both types show a single narrow U-shaped curve instead of the wavy one of Fig. 55. There are also rarer kinds of colour blindness generally due to disease of the eye. In most forms of colour blindness the sensation of white is retained, and the actual eye sensitivity to light and the shape of the photopic luminosity curve is little changed. It thus appears that the defect is not usually due to the total lack of certain types of light receptors; the coupled groups of receptors giving integrated sensations of white must be little disturbed, and the abnormality must reside in the isolated and rarer receptors which respond to the individual narrow bands in the spectrum. The proportion of the population who are markedly colour deficient is quite high, about 8 per cent., the incidence being much higher in males than in

females. About 1.2 per cent. are protanopes, 1.4 per cent. deuteranopes, and the remainder proto- or deuto-anomalous. In view of the serious mistakes which can arise when colour deficient persons perform tasks unsuited to them, the provision of suitable tests is important. Such persons can often distinguish strong colours under favourable conditions by intensity differences alone. Distinguishing tests are based on the discrimination of certain pale colours known to be easily confused by dichromats.

It has already been pointed out that one quantum of light destroys one molecule of visual purple (in solution). The limiting sensitivity of the human eye to wave-lengths of maximum luminosity is highest when the light is focused on a part of the retina about 20° from the fovea, where the receptors are almost entirely rods. The limit depends on the size of the retinal image. A point source of 1 candle-power can be just detected at 3 kilometres. The ultimate limit of sensitivity seems to be reached when 50–150 quanta of green light at $5,100 \text{ \AA}$ are received by the eye and concentrated on a minute image embracing about 500 rods. Of this light only about 10 per cent. is actually absorbed by the receptors, i.e. the eye responds to 5–15 single light quanta. Under these conditions the visual perception is fluctuating, and statistical analysis of the results shows that for a stimulus to be recorded several quanta must be simultaneously received by neighbouring receptors. The eye thus appears as an extraordinarily delicate though selective detector for radiation in the middle of the visual spectral range, rivalling the best photocells amplified electrically to the highest extent.

X

PHOTOCELLS

Conductivity Cells. These cells are made of thin deposits of selenium, or sometimes other semi-conductors, and their electrical resistance diminishes from 0.10–100 megohms to lower values when exposed to light. The property of 'semi-conduction' depends on the presence of 'impurities' in an insulator which have energy levels between the lower filled band and the upper 'conduction' band (p. 149). These 'impurities' may be foreign substances, or they may be a stoichiometric excess of anion or cation of the substance itself. Zinc oxide, for example, is a semi-conductor only when it has been heated so as to lose some oxygen; cuprous oxide, on the other hand, to show the same property, must be heated in oxygen so that it takes up an excess of that element. In semi-conductors of the ZnO type photoconductivity resembles that observed with insulators, i.e. electrons pass on excitation to the conduction band, but they come from the impurity levels, and not from the lower filled band, and hence the effect is shown with smaller energies and longer wave-lengths. In the Cu₂O type photoconductivity at long wave-lengths (visible and infra-red) depends on the presence of excess oxygen. Light causes electrons to pass to the impurity levels belonging to the excess oxygen, leaving behind a mobile 'positive hole' (atom or ion from which an electron is missing), which moves from ion to ion by exchange of charge with a velocity determined by the magnitude of the quantum absorbed. The complete separation of photo-electron and positive hole requires extra thermal energy when the absorbed light-quantum is small. Complicating effects are observed in practice, namely 'time lags' in the development of the photoconductivity and non-return to the exact original 'dark' resistance when the light is cut off. The

resistance change is not linearly proportional to the light intensity. Currents of 1,200 microamps. per lumen are obtainable (applied E.M.F. about 100 volts), and with special precautions 10^{-2} lumens of light may be measured to about 1 per cent. The spectral sensitivity of selenium conductivity cells has a maximum in the red and extends well into the infra-red.

Cells made of thallous sulphide are useful for special purposes since their response is to the infra-red 8,000–12,000 Å. When constructed free from time-lags they can be used at very low intensities by A.C. amplification.

Rectifier, Barrier, or Blocking-layer Cells are not so sensitive, producing up to 300 microamperes per lumen, but have the advantage of needing no external source of electric current. Their response is non-linear to light intensity, but is approximately so for external resistances as low as a few ohms. Their time-lag (due to capacity effects) is of the order of a few thousandths of a second. They are connected directly to a low-resistance microammeter for measuring purposes. The spectral range of some commercial cells is not very different from that of the eye, and they afford the simplest means of estimating light of moderate intensities.

The action of these cells is bound up with the process known as rectification which occurs at the boundary of metals and semi-conductors. The semi-conductor employed is cuprous oxide or selenium. A thin layer of cuprous oxide is formed on a copper plate, and by heat treatment is made to take up excess oxygen. This acts as an 'impurity' in providing new electron levels above the lower filled band of levels of 'pure' cuprous oxide. The back plate of copper acts as one electrode; the other is formed on the front surface usually by cathodic sputtering of a thin (transparent) deposit of metal, through which the light can pass. Either between the copper plate and the cuprous oxide or between the sputtered metal film and the oxide, depending on the type

of cell, is a very thin film (the blocking layer) of 'pure' cuprous oxide, having all its electrons in the lower filled band, and therefore an insulator. Rectifier cells have a spectral response at shorter wave-lengths than conductivity cells, and the primary process seems to be the transference by light-absorption of electrons from the lower filled band of the 'pure' oxide into the conduction band. These electrons pass into the adjacent metal electrode, being assisted by the potential difference set up by the capture of electrons from the metal by the 'impurity' levels of the neighbouring oxide. The leakage of the residual positive holes across the insulating layer gives rise to the electrical currents which these cells produce when exposed to light.

Emission Cells. The emission cell consists of a metallic layer (on the walls or on a plate) enclosed in a transparent bulb, connected to an external electrode; the other electrode, insulated from the first, is provided by a wire grid or ring in the bulb. The bulb is either highly evacuated or contains a small pressure of argon or sometimes, with potassium, hydrogen (gas-filled). When light falls on the metallic layer, electrons are liberated from the surface, and if the cell is connected to a battery (layer to —; ring electrode to +) a small current flows in the circuit.

The photoemission of electrons depends on their receiving quanta of energy large enough to enable them to break away from their forces in the metal and to leave the surface. A single-step process requires as a minimum about 46 kilo-calories per 6×10^{23} electrons (6,000 Å) for the alkali metals, 80 for zinc (3,500 Å), 92 kilo-calories for cadmium (3,000 Å), and 115 for platinum (2,500 Å). The wave-lengths given represent approximate spectral 'thresholds' for these metals. The facts of photoemission form one of the foundations of the quantum theory. Einstein pointed out that while the *number* of photoelectrons is proportional to the light intensity, the kinetic *energy* with which they leave the surface

depends only on the frequency of the light by the relation $\frac{1}{2}mV^2 = h\nu - h\nu_0$. ν_0 here represents the 'threshold' frequency for which electrons are able to leave the surface, and $h\nu_0$ the minimum work necessary just to take them out of the metal into a vacuum—the work function of the metal. Electrons which take up light 'photons' larger than this may leave the surface with a kinetic energy equal to the excess. The actual energy with which an electron leaves the surface, though important in this connexion, does not play any part in the functioning of photocells, since all electrons emitted are, or should be, drawn by a potential field towards the anode. For absolutely clean metallic surfaces the curve of photoemission rises from zero at the threshold to high values at shorter wave-lengths. Very commonly, however, the surfaces are deliberately contaminated to produce a thin layer of impurity. This makes emission a two-step process and allows it to occur below the threshold; the wave-length response shows an additional maximum at longer wave-lengths. Emission cells are therefore highly selective in their response to light, and examples of their sensitivity to wave-length is shown in Fig. 56. Cadmium or thorium (2,500–3,000 Å) and sodium (3,000–4,400 Å) are used for the ultra-violet region (in silica cell or with quartz window), potassium for general work in the visible region, and caesium where special sensitivity is required in the near infra-red. The two latter metals are always prepared with specially contaminated surfaces. They are deposited in extremely thin films on an oxidized silvered portion of the bulb (or a silver plate), the resulting film being a complex of silver, alkali metal oxide, and alkali metal (≈ 1 atom thick). Sometimes other non-metals than oxygen are used, but the details of preparations are kept secret and in any case are very difficult to reproduce in practice. Thin 'contaminated' film cells are much more sensitive and respond to longer wave-lengths than cells with pure alkali metals. Cells sensitive to the visible region can

be used for ultra-violet work if a suitable fluorescent screen is placed immediately in front of them. A screen composed of a single layer mosaic of clear potassium or ammonium uranyl sulphate crystals, for example, about 1 mm. thick, receives the ultra-violet light ($\lambda < 4,600 \text{ \AA}$), and between it and

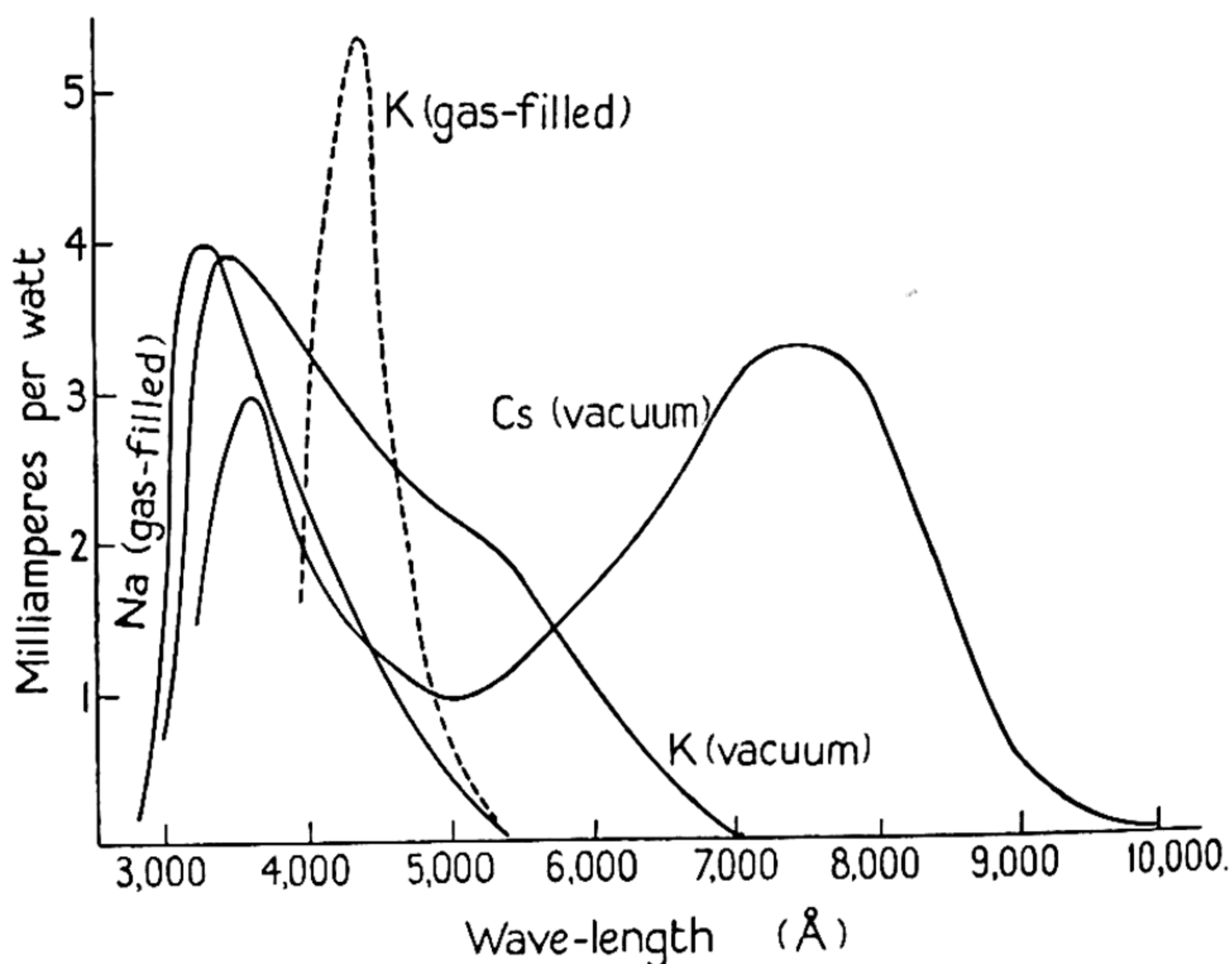


FIG. 56

the photocell is placed an Ilford Delta filter to cut off short-wave light passing between the crystals. The ultra-violet light is converted at a constant quantum efficiency into green fluorescent light of fixed wave-length distribution. Errors due to changes of reflection by the crystals at different wave-lengths may be minimized by containing them in a narrow cell filled with pure cyclohexane, and the combination then becomes a relative 'quantum counter' for the range 4,600–2,500 Å.

The primary current produced by a vacuum emission cell (K or Cs type) is about 30 microamperes per lumen. This is less than that from other types of photocell, but it is much

more easily amplified and measured. Because of this, emission cells have a much greater overall sensitivity to weak lights than rectifier or conductivity cells. The vacuum cell is a very stable and accurate device for measuring light especially suitable for moderately low intensities. It has no time-lag and is suitable for use with light fluctuating at very high frequencies. It needs a battery supplying about 30 volts; beyond this value the current is constant and very closely proportional to the illumination; below it the voltage is not sufficient to draw all the emitted electrons to the anode. In properly constructed cells there is no 'dark current' except with caesium cathodes, which have a thermionic emission at ordinary temperatures of about 10^{-13} amperes. When very faint lights are to be measured, cooling with solid carbon dioxide is used, which reduces the dark current to 10^{-15} amperes.

One method of magnifying the current from the cell is 'gas-filling'. The primary electrons are caused to ionize the gas by collision, liberating many secondary electrons and increasing the current up to ten times or more. Such a cell has very different electrical characteristics from the vacuum cell. The current increases with the voltage, which must be higher (about 160 volts for potassium and 90 volts for caesium) and which must not exceed a limiting value (lower the higher the illumination) beyond which a destructive glow discharge occurs in the cell. To minimize the effect of this, a 100,000 ohm resistance is used in series with gas-filled cells. Gas-filled cells are not reliable for accurate work; they have a response not quite linear to light intensity, and cannot be used for fluctuating lights above 30,000 per sec., as occur in cinema or television practice.

'Secondary emission' cells give a greatly increased current without any of the disadvantages of gas-filled cells. The primary electrons are caused to impinge on a target coated with an electron emissive material, generally the same as

that of the photosurface. Each electron liberates about four others by impact, and nine-stage 'electron multipliers' have sensitivities over 1 amp./lumen, with an overall magnification of 30 million on primary currents $< 10^{-16}$ amp. For work with very feeble light rubidium is preferable to caesium owing to its freedom from 'dark current'.

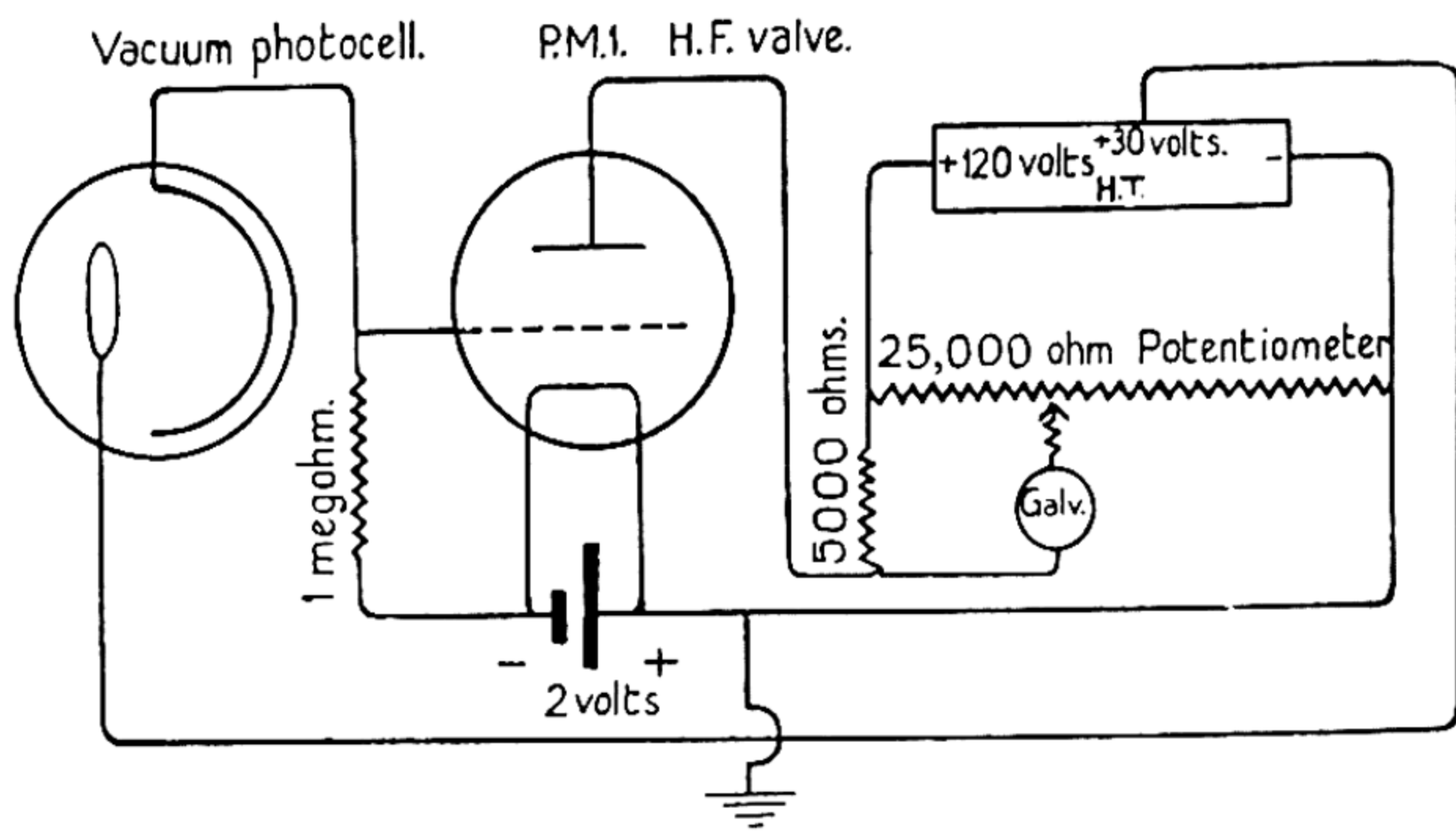


FIG. 57

For the measurement of light intensities met with in work making use of optical instruments (photometers, etc.) an ordinary type vacuum photocell amplified by a valve with potentiometer balanced anode current is convenient. A circuit is shown in Fig. 57. More accuracy is obtained with an electrometer valve sealed with the photo-cell in an outer evacuated envelope to eliminate leakage effects due to moisture. The most sensitive cells available contain the substance SbCs_3 , and liberate one electron per five incident quanta at their optimum wave-length in the blue-green. Their wave-length response, however, is very narrow. Intensities as low as 10^{-7} foot-candles can be measured to 2-5 per cent. with such cells amplified with a valve. Caesium-bismuth cells have a wider spectral range with somewhat lower sensitivity; the best potassium cells are about $\frac{1}{20}$ as sensitive in the blue region of the spectrum. When extremely

low intensities are to be measured, as in astronomical or phosphorescence work, special precautions must be taken in electrical screening, and the electrometer valve is employed in a balanced circuit to eliminate small changes in both filament and high-tension voltages. Another method is to use an electrostatic circuit, care being taken to reduce errors due to atmospheric moisture effects. Instead of using a circuit based on the simple one of Fig. 57 the photocell may be connected to the valve grid (or to an electrometer) without a leak to earth and the rate of charging up of the system measured. In accurate work care must be taken to see that the distribution of light over the sensitive surface remains unchanged as the sensitivity commonly varies over the surface. Sensitivities of $10^3/\rho - 10^2/\rho$ quanta/sq.cm./sec., where ρ is the apparent 'quantum efficiency' of the photocell surface, are obtainable with a Hofmann electrometer or an electrometer valve and a suitable cell. ρ varies from 0.01 for 'contaminated surface' cells to 0.2 for the compound SbCs_3 at their optimum wave-lengths. At the highest sensitivities both electrometers and D.C. valve amplification methods are very temperamental. A.C. valve amplifiers (with a revolving sector to modulate the light) are more robust, but about ten times less sensitive, their limit of detection being about 10^{-16} amp. (= 600 electrons/sec.) Above 10^{-13} amp. both A.C. and D.C. amplification is easy and steady.

A comparison of ultimate sensitivities of light recorders is interesting. The eye can just detect about 150 quanta/sec. in the green region. The emission photocell with the highest possible amplification and at its optimum wave-length will detect $10^2 - 2 \times 10^4$ quanta/sec., depending on the emissive material. Rectifier type photocells need 2.5×10^{10} quanta/sec. for minimum response on a sensitive galvanometer. The photographic plate in the blue region will detect 10^2 quanta/sec. concentrated on a spot, or 10^5 quanta/sq. cm./sec. on the plate, but needs 15,000 secs. exposure to produce this result.

In practice it proves the most sensitive agent for registering weak lights of long duration, in spite of 'reciprocity law failure' (p. 233), owing to its power of integrating light over time intervals. The thermopile, which has the advantage of uniform energy sensitivity over all wave-lengths, and which can be used in the infra-red region, is vastly less sensitive. In the visible region, for a minimum response, it requires 2.5×10^7 quanta/sec. concentrated on a spot, or 10^{10} quanta/sq. cm./sec. In spite of its insensitivity its freedom from selectivity often recommends its use for certain types of work, and of course for infra-red work it is essential.

Geiger counters consist of a quartz tube containing hydrogen at a low pressure, thinly platinized inside, with an insulated axial wire of specially prepared surface maintained at a very constant appropriate voltage about 1,000 volts + to the platinum. Light in the far ultra-violet, capable of liberating photoelectrons from the platinum, can be detected at intensities corresponding to a few photons per second. Cathodes of cuprous iodide are very effective for the region 2,600–1,900 Å. Each photoelectron causes a breakdown in the insulation of the gas in the cell whereby a comparatively large current flows momentarily. The sensitivity is limited by the random arrival of cosmic rays, which produce electrons in the cell at the rate of a few per second. Attempts have been made to construct Geiger counters with an active alkali metal surface which would be sensitive to visible radiation. A sensitivity of about one electron per sq. cm. per second might be expected, and this would provide a means of measuring low light intensities both much more sensitive and less delicate in manipulation than any now available. There are experimental difficulties in satisfying the conditions necessary to prepare surfaces very responsive to light which are also suitable for the electrical conditions of the counter, which needs an oxidized anode and a reduced cathode.

XI

CHEMILUMINESCENCE

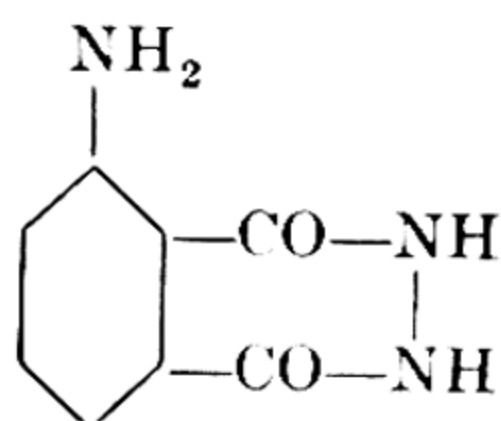
DURING vigorous chemical reactions, and particularly in oxidations, excited molecules are formed of which a proportion may escape deactivating influences and lose their energy by the emission of visible radiation. Flames of burning substances show spectra which arise from such processes. Smoky flames, with solid particles present, as that from a coal-gas bat's-wing burner, produce a continuous spectrum approximating to that from a 'black body', which gives no information about the energy levels of the emitters. Such emission is classed as temperature radiation. Burning sulphur or phosphorus also show continuous spectra, but they have a different energy distribution from temperature radiation, and indicate true chemiluminescence. Their lack of structure may be attributed to disturbance of energy levels of the emitters under the conditions existing in the flame, so that overlapping occurs among the very great number of lines emitted. At lower pressures, as when traces only of sulphur or phosphorus in the presence of hydrogen are burnt in air, a banded spectral structure appears. Phosphorus shows similar bands in its remarkable glow when oxidizing at ordinary temperatures. Metals, such as sodium, added in traces to a flame, emit their characteristic atomic spectral lines through receiving energy from the hot gas, and from copper or strontium chlorides in the flame structured bands characteristic of excited radicals (CuCl and SrCl) are visible. The limits separating chemiluminescence from emission due to heat alone, and from electronic excitation (as in a vacuum tube), are not as clearly marked as they might be expected to be; the distinction is made by considering the applicability of Kirchhoff's law (Chap. II).

Some flame spectra show an extensive rotational and

vibrational structure from which accurate information about the moments of inertia, vibrational constants, and electronic levels of the emitters may be obtained. A diatomic emitter is easily characterized by its simple rotational fine structure, and its derived moment of inertia generally enables it to be identified. As examples of such simple cases, the emitter of bands in the oxyhydrogen flame has been identified with the OH radical; in the ammonia-oxygen flame with the NH radical; in the blue part of a Bunsen burner (coal gas) with the CH radical; in the green part of a Meker burner with C_2 molecules; and in a hydrogen flame containing a little sulphur with S_2 molecules. Similar bands, as well as others due to excited ions and other radicals, are produced by the excitation of vapours at low pressures in vacuum tubes. In many other systems, as in the glow of phosphorus, the emitter cannot be so simply discovered, and the process by which it receives its energy is often obscure. The emitter may obtain its excitation directly through chemical action with another molecule by being formed from the union of two radicals present in the reaction, or by collisions from newly formed molecules of high energy. It is sometimes not easy to find criteria to distinguish between these mechanisms.

The efficiency of chemiluminescent processes in condensed systems is generally very low, and in gases it is rarely high except under conditions of very low pressure. This may be because very few of the molecules capable of emission are raised to sufficiently excited levels, or due to extensive deactivation processes. Light of extremely high intensity would be emitted if all the reacting molecules emitted in the visible region. If one gram molecule of a substance chemically reacted in one second, and every molecule emitted a quantum of yellow light at the point of maximum sensitivity of the eye, the intensity would be 100 million lumens. At this wave-length 670 lumens correspond to 1 watt. Any spreading of the emitted light over other wave-lengths would reduce

its brightness to the eye. It is therefore remarkable that a mixture of carbon bisulphide vapour and nitric oxide, when ignited, produces light of intensity of 83 lumens per watt. As the emission is rich in ultra-violet as well as visible rays a very high percentage of the energy of this reaction must appear as light. The emitter appears to be S_2 , but the spectrum is continuous at ordinary pressure. In the glow of phosphorus under ordinary conditions not more than one molecule in 2,000 oxidizing emits energy as light, and the luminous efficiency of the glow in air at the ordinary temperature is only 10^{-3} lumens per watt of total energy liberated. The use of the term 'cold light' in connexion with this reaction is therefore far from correct. A very interesting example of chemiluminescence is the oxidation by permanganate of certain solid derivatives of silicon, on the surface of which fluorescent dyes such as rhodamine B have been absorbed. Here the fluorescent spectrum of the dye is very strongly emitted, showing that the energy of oxidation of the solid surface is transferred to the adsorbed dye molecules, which are raised to other excited levels. Most examples of chemiluminescence prove to be of a type where the light is not emitted directly by the reacting molecule, but by some other molecule of a fluorescent nature to which the energy is first transferred. A number of oxidations of organic compounds in the vapour state or in solution, at temperatures at or not far above the normal, take place with light emission, among which may be mentioned formaldehyde, pyrogallol, aesculin, a number of sulphur and phosphorus compounds, and the phthalic cyclo-hydrazides. O-amino phthalic cyclic hydrazide,



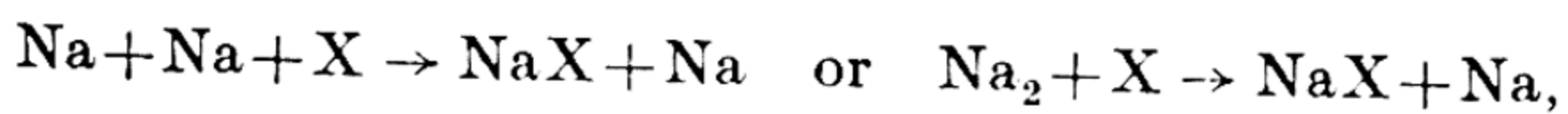
oxidized by ferricyanide or hypochlorite solutions when dissolved in alkali containing a little hydrogen peroxide, emits a blue light, perceptible at dilutions of 1 in 10^8 , and strong enough to be seen in sunlight at higher concentrations. A maximum of about one light quantum per 300 molecules reacting is emitted. The chemiluminescent spectra of these cyclo-hydrazides resemble in some respects their characteristic fluorescent spectra, whence it follows that the emitter must be a molecule of structure not very different from that of the original substance. The mechanism of the oxidation has been the subject of study and appears to involve the formation of intermediate peroxides.

The oxidation of dimethyldiacridylum salts under appropriate conditions causes the emission of a bright green glow, recognizable in 1 part in 10^{10} .

The emission of light by living organisms is always due to oxidation processes, which in some examples can be shown to arise from an oxidation of 'luciferin', of unknown structure, under the influence of an enzyme 'luciferase'. The emission appears to come not from the oxidized substance but from a fluorescent group of the luciferase, and has a smooth intensity-wave length curve reminiscent of the retinal curves of the eye (p. 243). Bioluminescence is very irregularly distributed over the animal and vegetable kingdoms, and appears to be an accidental variant of one of the many oxidation mechanisms of the living cell. In the higher forms of life, such as deep-sea fishes, fire-flies, or glow-worms, the light emission has been developed to serve the organism and to function in a controlled manner. Luminous bacteria, which cause the luminescence of decaying fish, glow constantly with a more feeble light than that of the controlled processes above. Rotting wood sometimes glows through the presence of a luminous fungus, while the luminescence of the sea is due to a host of organisms, of which the protozoa *Noctiluca*, and the crustacean *Cypridina* and jelly-fish may be

noted. The overall efficiency of light production is difficult to estimate owing to the simultaneous occurrence of other non-luminous oxidations, but does not appear to exceed that of ordinary illuminants.

A chemiluminescent reaction which can be analysed into elementary stages is that between sodium and the halogens or halogen-containing molecules such as CH_3Cl or HgCl_2 . An extensive study of these reactions has been made by Polanyi and collaborators. The halogen is introduced through a nozzle into a space containing sodium vapour, pressures in the system being about 0.01 mm. corresponding to a time between collisions of about 10^{-4} sec. Emission of the yellow *D* lines of sodium occurs with an efficiency which may rise to near unity for chlorine and is much lower for reactions with organic or inorganic halides. For the first stage of the reaction we must have $\text{Na} + \text{X}_2 \rightarrow \text{NaX} + \text{X}$ (X = halogen) followed by reaction of sodium with the halogen atoms formed. A non-luminescent wall reaction $\text{Na} + \text{X}$ occurs which may be minimized by using a high sodium concentration. The same reaction cannot occur in the gas phase without the intervention of a third molecule to carry away excess energy. In presence of the excess of sodium, therefore, we have



since Na atoms readily combine to give Na_2 molecules on collision. This reaction gives out much more energy than that above, since the energy necessary to dissociate the halogen molecule is not required, and the energy of dissociation of Na_2 is small. At some stage sodium atoms are excited, whereby they emit the *D*-line radiation (48.5 kilo-calories per gram atom) after an interval of about 10^{-8} seconds. There are two possibilities: one is that the above reaction is $\text{Na}_2 + \text{X} \rightarrow \text{NaX} + \text{Na}^*$, followed by $\text{Na}^* \rightarrow \text{Na} + h\nu$, and the other is $\text{Na}_2 + \text{X} \rightarrow \text{NaX}^* + \text{Na}$ followed by $\text{NaX}^* + \text{Na} \rightarrow$

$\text{NaX} + \text{Na} + h\nu$. At first sight the first of these appears more likely, as being simpler, but there are reasons why the latter is preferred. The chemiluminescence is quenched by foreign gases more strongly than is the resonance emission of the *D* line of sodium, indicating the retention of the activation energy by some other molecule for a longer period than 10^{-8} seconds. Also a faint emission of sodium lines of shorter wave-length than the yellow is observed, showing that energy from repeated collisions can accumulate on one molecule. In view of the short radiation time of the excited sodium atom this could not happen with the first possible reaction. It is therefore concluded that emission occurs after excitation of sodium atoms by collision with NaX molecules of high energy. This energy must be vibrational, as electronic energy is too great to be possible, and rotational (or translational) energy is not efficiently transferred on collision. This is most clearly brought out by the sodium-iodine reaction. Here the reaction $\text{Na}_2 + \text{I} \rightarrow \text{NaI} + \text{Na}$ has an energy liberation of only 1 kilo-calorie above that necessary to excite the Na atom, and yet a light yield (quanta emitted per two atoms of sodium reacted) of 40 per cent. is observed. If the assumed mechanism of the reaction is correct it must be concluded that almost all the energy of reaction remains on the NaI molecule in the form of vibrational energy, so as to be available for subsequent transference as electronic energy to the Na atom. A potential-energy surface interpretation of this may be given. We construct the supposed energy surface for the reaction of an atom with a diatomic molecule as described on p. 198. Fig. 58 shows the shapes necessary. A vertical plane erected on *YZ* at a great distance along *OY* cuts the contours to reproduce the two-dimensional potential-energy curve of the molecule Na_2 , while one on *AZ* a great distance along *OA* gives the curve of the molecule NaI. The surfaces contoured on the diagram refer to the energies of interaction of the three atoms at different distances, and arranged in a

line. The approach of an iodine atom to a molecule Na_2 is represented by the ascent of the valley from B to the col X (the activated state). This col does not enter the valley leading down to C (reaction products) at the head, as in Fig. 47, but at the side, so that the energy of the activated state is not

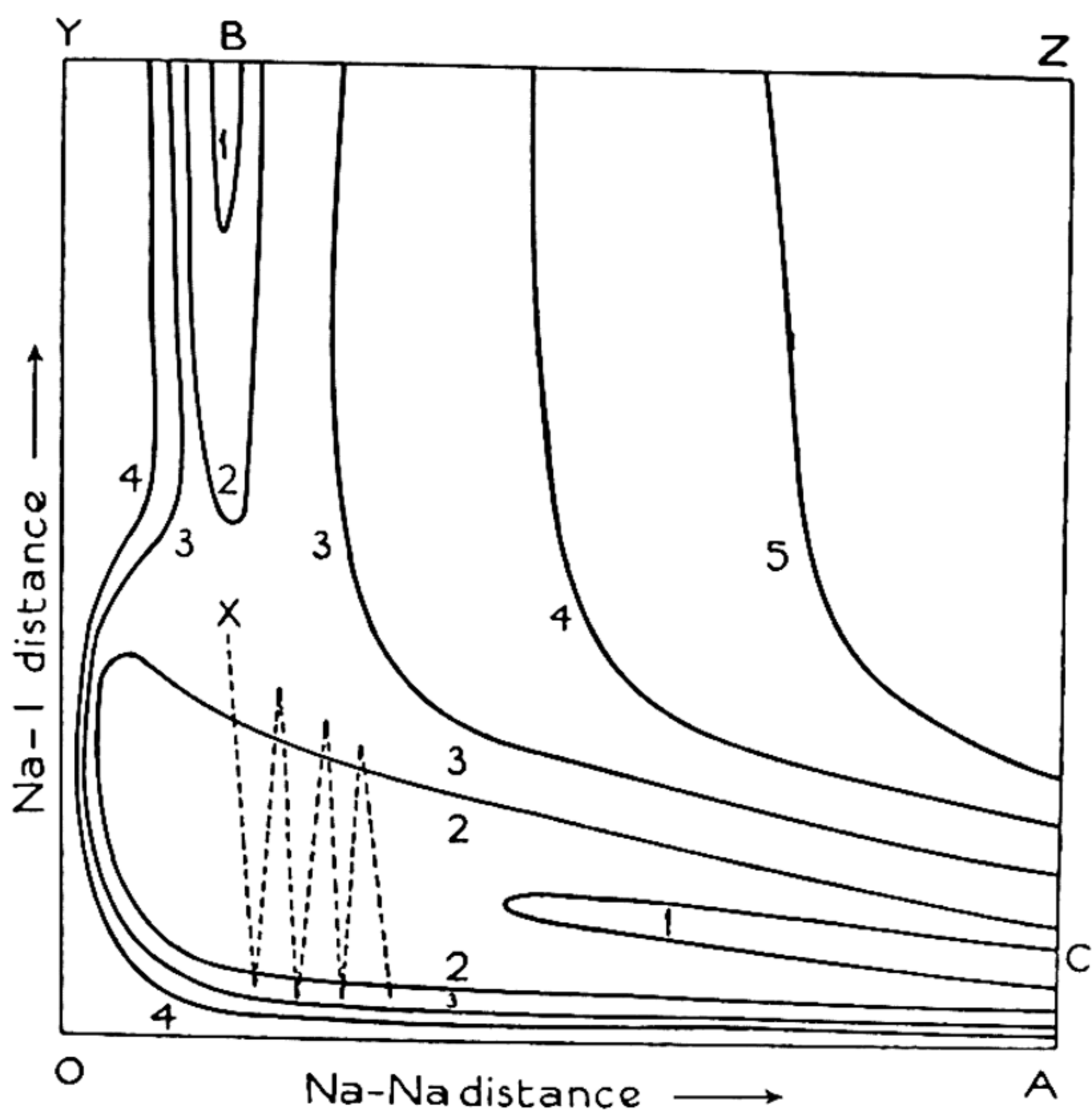


FIG. 58

employed in mutual repulsion of the products with high translational energy, but appears as vibrational energy as indicated by the dotted line. The analogy of a frictionless marble moving on the contours illustrates the behaviour of the system. An examination of the system by the theory of reaction rates (p. 197) shows that while the larger part of the Na atoms are thus indirectly excited some are excited directly. This may diagrammatically be represented by

intersecting potential energy surfaces of the nature of those in the two-dimensional Fig. 42.

This reaction has been dealt with in some detail to show how even in well-investigated chemiluminescent reactions of an elementary character the results are neither simple nor conclusive, but that, as evidence for the mechanisms proposed grows more certain, very interesting deductions about energy interchanges between atoms and molecules may be made.

A chemiluminescence of quite a different type has been the subject of certain investigations. It is found that almost any chemical reaction in condensed systems gives off very feeble radiations between 2,400 and 2,000 Å, about 1 quantum per 10^{15} to 10^{14} molecules reacting. These are minimum values, limited by the wave-length sensitivity and the effective quantum efficiency of the detector used—a Geiger counter. The most probable source of this radiation is the chance accumulation of high energies by a minute fraction of the molecules through successive energy transfers from chemically activated molecules; they thus reach electronic levels near 2,000 Å, where practically all substances absorb strongly, and emit the radiation which is detectable by the extremely delicate method employed.

Of similar character is the 'mitogenetic radiation' given off in living cell processes and in fermentations, and detected by its biological effects on the mitosomes of cells. In some cases, if not in all, atmospheric oxygen is necessary for the emission to be shown, and visible light is also required sometimes. The wave-length of the radiation varies with traces of certain impurities added, and its origin cannot be simple. Probably the high energy required originates from the oxidation of traces of substances with free valencies formed in infinitesimally small amounts as side reactions, the oxidation being either thermal or photochemical. The reaction product molecule transfers its energy (≈ 150 kg. cal. per mole) to some other molecule present which is capable of fluorescence, and

the radiation emitted is characteristic of the latter molecule. Owing to the minute quantities of radiation emitted and to the difficulties of its detection and analysis, and to the inapplicability of chemical methods of corresponding delicacy, the subject of radiations of this type is one of peculiar obscurity.

APPENDIX I

FILTERS FOR THE ISOLATION OF LINES OF DISCHARGE LAMPS

<i>Wave-length, Å</i>	<i>Filter combination I (Glasses and solutions)</i>	<i>Alternate filter combination II for the preparation of gelatine film filters. Figures are in grams per sq. metre of film</i>
5,890 Na 5,896	Chance OY 1, 2 mm. Chance OB 2, 1 mm.	Tartrazine 3 Astraphloxine FF extra 0.5 Thionine Blue GO 0.05
6,362 Zn	Chance OR 2, 2 mm.	Tartrazine 3, Fast Red D 1
4,811 4,722 Zn 4,680	Chance OB 2, 4 mm. Chance OY 8, 2 mm.	Filter Blue II 1 Thionine Blue GO 0.2
3,076 Zn	Corning red purple corex. 9863, 5 mm. Solution of 303 gm. NiSO ₄ . 7H ₂ O + 86.5 gm. CoSO ₄ . 7H ₂ O in 1 litre, 20 mm. Solution of picric acid, 0.16 gm. per litre, 20 mm.	
6,438 Cd	Chance OR 1, 2 mm.	Tartrazine 3 Astraphloxine FF extra 1.5
5,086 Cd	Chance OY 4, 2 mm. Chance OB 2, 2 mm.	Rapid Filter Yellow 6 Patent Blue 0.2
4,800 Cd 4,678	Chance OB 2, 5 mm. Chance OY 8, 2 mm.	Filter Blue II 3 Thioflavine 0.5
3,261 Cd	Corning, 774 Ni—Co solution as for 3,076 Zn Solution of K ₂ CrO ₄ , 0.15 gm. per litre, 20 mm.	
5,790 Hg 5,777	Chance OY 1, 2 mm. Chance OB 2, 1.5 mm.	Tartrazine 3 Eosin 1 Thionine Blue GO 0.3
5,461 Hg	Chance OGr 1, 2 mm. Chance ON 16, 2 mm.	Tartrazine 3 Patent Blue 0.2 Chance ON 16, 2 mm.
4,358 Hg	Chance OB 1, 3 mm.	

Wave-length, \AA	Filter combination I (Glasses and solutions)	Alternate filter combination II for the preparation of gelatine film filters. Figures are in grams per sq. metre of film
4,047 Hg	Chance OB 1, 2 mm. Chance OV 1, 1 mm.	
3,650 3,663 Hg	Chance OX 1, 4 mm.	
3,341 Hg	Schott UG 2, 2 mm. Schott GG 2, 2 mm. N/5 Nitric acid solution, 20 mm.	
3,126 3,132 Hg	Corning 774 K_2CrO_4 solution as for 3,261 Cd	
5,350 Tl	Chance OGr 1, 2 mm. Chance ON 16, 2 mm.	Tartrazine 3 Toluidine Blue 0.3 Thionine Blue GO 0.05
4,216 4,202 Rb	Chance OB 1, 2 mm.	Fuchsine 0.5 Thionine Blue GO 0.5
4,593 4,555 Cs	Chance OB 1, 2 mm. Chance OY 9, 2 mm.	Filter Blue II 1.5 Thionine Blue GO 0.2

To remove the infra-red, filter combinations I require the following additional filters:

Chance ON 13, 2 mm. = X.

Solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 57 gm. per litre, 10 mm. = Y.

Water, 20 mm. = Z.

For 5,890/6 Na, 4,800/678 Cd, 5,086 Cd, 5,790/77 Hg, 5,461 Hg, and 4,047 Hg, Y.

For 6,362 Zn and 6,438 Cd, X.

For 3,132/26 Hg, Y.

For 4,811/680 Zn, 4,358 Hg, and 3,663/50 Hg, Z.

Filter combinations II require Y, or for blue-green lines, a film of Filter Blue-Green.

APPENDIX II

MERCURY LAMP FILTER SOLUTIONS FOR PHOTOCHEMICAL PURPOSES

(Note: Nickel, cobalt, and copper solutions must be very free from iron, and the first two from chloride.)

- A. Copper chloride, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 1,000 gm. in 1 litre water.
- B. Calcium chloride, 3 molar, i.e. 333 gm. anhydrous salt made up to 1 litre solution with water (acidified).
- C. Potassium dichromate, 15 gm. in 200 c.c. water.
- D. Neodymium nitrate, 30 gm. made up to 100 c.c. solution with water.
- E. Copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 25 gm., 300 c.c. ammonium hydroxide ($d = 0.88$), made up to 1 litre with water.
- G. Copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 125 gm. made up to 1 litre with water.
- H. Copper nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 200 gm. in 100 c.c. water.
- J. Iodine, 0.75 gm. in 100 c.c. carbon tetrachloride.
- K. Sodium nitrite, NaNO_2 , 75 gm. in 100 c.c. water.
- L. Nickel sulphate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 350 gm., cobalt sulphate, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 100 gm., made up to 1 litre with water.
- M. Potassium hydrogen phthalate, 5 gm. in 1 litre water.
- N. Copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 15 gm. in 1 litre water.
- P. Potassium iodide, KI, 1.7 gm. in 1 litre water.
- R. Potassium iodide, 0.14 gm., Iodine, 0.1 gm. in 1 litre water.
- S. Cobalt chloride, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 30 gm. in 100 c.c. of 3M calcium chloride solution.
- T. Nickel sulphate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 82 gm. in 100 c.c. of 0.25M copper sulphate solution.
- U. 220 gm. $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ + 200 gm. $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ in 1,000 gm. solution.
- V. 120 gm. $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ + 23.5 gm. $(\text{NH}_4)_2\text{SO}_4$ + 82.8 gm. aq. NH_3 ($d = 0.925$) in 1,000 gm. solution.
- W. Gaseous chlorine at 1 atmosphere in a fused silica cell 3 cm. deep.

USE OF FILTER SOLUTIONS

<i>Mercury line, Å</i>	<i>Filter combinations</i>
5,790 5,777	10 c.c. <i>A</i> with 90 c.c. <i>B</i> , 1 cm., combined with either <i>C</i> , 2 cm., or Chance glass OY 1, 2 mm.
5,461	20 c.c. <i>A</i> with 80 c.c. <i>B</i> , 1 cm., combined with either <i>D</i> , 1 cm., or Chance glass ON 16, 2 mm.
4,358	<i>E</i> , 2 cm., combined with <i>K</i> , 1 cm., or <i>H</i> , 2 cm., combined with <i>K</i> , 1 cm. (Transmits a little 5,461 Å.)
4,047	<i>H</i> , 2 cm., combined with <i>J</i> , 1 cm.
3,650 3,663	<i>G</i> , 1 cm., combined with Chance glass, OX 1, 2-3 mm.
3,132	<i>L</i> , 3-4 cm., combined with <i>M</i> , 1 cm., or <i>U</i> , 2.5 cm., combined with <i>V</i> , 2 cm., and <i>M</i> , 1 cm.
3,340-3,000	<i>S</i> , 1 cm., combined with <i>T</i> , 1 cm.
3,340-2,895	<i>L</i> , 3-4 cm., combined with <i>N</i> , 1 cm., or <i>U</i> , 2.5 cm., combined with <i>V</i> , 2 cm., and <i>N</i> , 1 cm.
2,650	<i>L</i> , 3-4 cm., combined with <i>P</i> , 1 cm., and with <i>W</i> , 3 cm., or <i>U</i> , 2.5 cm., combined with <i>V</i> , 2 cm., and with <i>P</i> , 1 cm., and <i>W</i> , 3 cm.
2,650-2,537	<i>L</i> , 3-4 cm., combined with <i>W</i> , 3 cm., or <i>U</i> , 2.5 cm., combined with <i>V</i> , 2 cm., and <i>W</i> , 3 cm.
2,537	<i>L</i> , 3-4 cm., combined with <i>R</i> , 1 cm., and with <i>W</i> , 3 cm., or <i>U</i> , 2.5 cm., combined with <i>V</i> , 2 cm., and with <i>R</i> , 1 cm., and <i>W</i> , 3 cm.

Solutions *E*, *M*, *P*, and *R* should be frequently renewed.

APPENDIX III

OTHER FILTER DATA

(Filters should be made up with the aid of a spectroscope. The transmission limits given are only approximate, and can be varied by changing the concentration of the filter.)

Removal of Infra-red

1 cm. of 10% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Chance glass ON 13.

Removal of Ultra-violet

1 cm. acetic acid, 4N, cuts off at 2,400 Å.

0.01 mm. mica cuts off at 2,800 Å.

1 mm. glass cuts off about 3,100 Å.

1 cm. copper sulphate, 1.5%, cuts off at 2,750 Å.

Ditto, 15%, cuts off at 2,900 Å.

1 cm. ferric alum in 2N H_2SO_4 , 1%, cuts off at 3,800 Å.

Dufay Chromex 2324 or Ilford 805. Chance glass OY 9 or OY 10.

2 cm. of cupric nitrate sat. transmits 5,500–3,700 Å.

Filters cutting off Ultra-violet and Short-wave end of visible spectrum

0.5 cm. of sodium nitrite sat.	removes all beyond 4,200 Å.
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0.5 cm. potassium chromate 2%	„ „ 4,850 Å.
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0.5 cm. picric acid sat.	„ „ 4,900 Å.
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0.5 cm. potassium dichromate sat.	„ „ 5,350 Å.
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0.5 cm. chromium trioxide sat.	„ „ 5,900 Å.
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Other suitable yellow filters transmitting red, yellow, and green are tartrazine, aurantia, or filter yellow K, 2 mm. sat. solution in water; or *p*-nitrotoluene in alcohol.

Filters cutting off Long-wave end of visible spectrum

Cuprammonium sulphate solution 5 to 50 gm. copper sulphate,
300 c.c. strong ammonia solution, 700 c.c. water, 1 cm.

Copper nitrate sat. 2 cm. (see above).

Filter Blue-green solution.

Copper sulphate sat.

Filters for Spectral bands. (See also pp. 291 and 292.)

Infra-red. Glass absorbs wave-lengths longer than 20,000 Å. Iodine in CS_2 , thin ebonite, or Wratten or Kodak filters (I.R.), or Chance glass OX 2, 3, or 4 transmit i.r. only.

Red. Crystal violet 5BO, dilute solution in water, 1 cm. (or methyl violet in alcohol, or rhodamine B in water, dilute), combined with 1 cm. of picric acid or potassium dichromate solution.

Yellow. See above for yellow filters (also transmitting red which may be removed by a filter of strong copper sulphate).

Acidified mixture of copper sulphate and potassium dichromate solutions 200 gm. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ + 290 gm. CaCl_2 (anhydrous) made up to 1 litre, 1 cm., combined with 2 cm. of potassium dichromate, 75 gm./litre, transmits 6,400–5,550 Å.

Yellow-green. Above copper-calcium chloride filter without dichromate filter. 50 gm. $\text{K}_2\text{Cr}_2\text{O}_7$, 12 gm. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 3 cm. conc. H_2SO_4 + 1 litre water transmits 5,750–5,800 Å.

Green. 100 c.c. nearly sat. CrO_3 solution + 400 c.c. nearly sat. cupric nitrate solution, 2 mm., transmits a band with mean at 5,850 Å.

Naphthol green B, 1/1,000 in water, 5 mm., transmits a band with mean at 5,400 Å.

Cupric chloride sat. 2 cm., transmits 5,700–4,950 Å.

Blue-green. Light green, brilliant green, or malachite green, 1/1,000 (remove red transmitted by cupric nitrate filter), transmit in the range 5,400–4,500 Å. A tartrazine filter in addition narrows the range by cutting off the blue.

Blue. Cuprammonium solution containing potassium chromate. (The latter if added in suitable amount removes the violet.)

Night-blue, 1/1,000, transmits 5,000–4,000 Å.

Crystal violet, dilute, combined with a filter of cupric chloride, 250 gm./litre.

Victoria blue, 0.085%, 0.5 cm.

Blue-violet. Methyl violet or crystal violet, dilute, combined with a cupric nitrate or sulphate filter to remove red.

Violet. Iodine in CCl_4 , 7.5 gm./litre, 1 cm., transmits 4,300 to near ultra-violet. Red and ultra-violet removed by 1 cm. of cupric nitrate sat.

Ultra-violet. See Appendix II. (Ni—Co and Cl_2 filters, etc.)

Also: 3 mm. plate of KCl heated *in vacuo* and bombarded with cathode rays removes visible and transmits 4,000–2,300 Å.

0.5 mm. CS_2 transmits 2,900–2,650 and the visible to 3,600 Å.

Gaseous bromine absorbs the short-wave end of the visible spectrum and transmits in the ultra-violet.

APPENDIX IV

PHOTOCHEMICAL TECHNIQUE TO DETERMINE QUANTUM EFFICIENCY

THE light beam should be approximately parallel and of a diameter somewhat smaller than the face of the photochemical cell. Immediately behind the cell is placed a thermopile. The linear form is best, fitted with a 1 mm. slit very close to the junctions. It is moved 1 mm. at a time across the light beam to give the sum of the total energy in the beam. The thermopile should have a crystalline quartz window, and be calibrated with its galvanometer against a standard lamp of known energy emission. If it is necessary to reduce the sensitivity of the combination, a shunt resistance s and series resistance a such that $a = p^2/(p+s)$, where p is the thermopile resistance, is employed with the galvanometer. The ratio of energies falling on the thermopile at equal deflexions for reduced sensitivity to that when $a = 0$ and $s = \infty$ is $1+p/s$.

Let the summed thermopile readings be A with cell removed, B with cell filled with water, and C with cell filled with aqueous solution. From time to time during the exposure the cell is removed and a value of A determined. Fluctuations of the lamp will cause it to vary, and its average value is taken. The ratio A/B is a constant K under steady light conditions. Then energy incident on liquid in cell after penetrating the transparent silica wall

$$= \frac{(1-0.085)B}{(1-r_p)(1-r)10^{-wd}} = RB = RA/K.$$

$(1-0.085)$ = average transmission of calibrating standard lamp energy through quartz window of thermopile; $(1-r_p)$ = transmission of the same to the photochemical light; $(1-r)$ = transmission of one window of cell when filled with water; w = absorption by water, and d = the thickness of the cell. Values for these quantities are given in the table below:

Wave-length, A	$(1-r_p)$	$(1-r)$	R	w
4,358	0.909	0.94	1.074	0
3,660	0.905	0.94	1.078	0
3,132	0.897	0.938	1.087	0
2,650	0.885	0.934	1.16	0.009
2,537	0.880	0.933	1.21	0.012

Then energy absorbed in time t

$$= \frac{RA t}{K} \left(1 + \frac{rCK10^{-ud}}{A} \right) \left(1 - \frac{CK10^{-ud}}{A} \right)$$

allowing for back reflection within the cell.

This quantity is converted to units of $Nh\nu$, and the ratio (chemical change in gram-molecules)/ $Nh\nu$ = quantum efficiency.

Where the photochemical cell is immersed in a thermostat and contains gas, the formula must be modified. See references of Chap. VI.

Instead of the thermopile chemical actinometry may be employed in the ultra-violet region. Solutions of uranyl oxalate containing excess oxalic acid decompose photochemically to give carbon dioxide and monoxide. The stock solution should contain 3.75 gm. uranyl oxalate (made by mixing hot solutions of oxalic acid and uranyl nitrate, drying *in vacuo* and then for 3 hours in air at 110° C.) and 6.3 gm. oxalic acid in 1 litre. For wave-lengths 4,350–3,300 Å the solution may be used as such, but for the region 3,300–2,500 Å it is better diluted up to one-tenth. The solution is titrated by weight against N/10 (or more dilute) permanganate at 80° C. after adding about one-third of its volume of 9N H₂SO₄, and again in the same way after exposure to the light, using the acid to wash out the cell. The number of $Nh\nu$ falling on the solution in the cell during the exposure time is then given by:

$$\frac{\text{N/10 KMnO}_4 \text{ titre difference (c.c.) of cell contents before and after exposure}}{(\text{quantum efficiency})(\text{absorption}) \times 2 \times 10^4}$$

Values of the quantum efficiency and absorption are given in the table:

Wave-length, \AA	Quantum efficiency	Light absorption fraction in 1 cm. cell thickness
stock solution { 4,350	0.57	0.242
4,050	0.56	0.284
3,650	0.48	0.342
solution diluted to one-tenth { 3,135	0.55	0.658
3,030	0.56	0.82
2,650	0.57	1.0
2,540	0.60	1.0

The solution should be stirred during illumination and the amount of change should not exceed 50 per cent.

APPENDIX V

EXPERIMENTS WITH LIGHT OF CHEMICAL INTEREST

PHOTOCHEMICAL EXPERIMENTS

1. *Photodecomposition of uranyl oxalate.* Directions for this reaction are given in Appendix IV. A parallel-walled glass or silica cell holding 10–20 c.c. of solution should be used for the exposure if quantitative results are wanted. Light from a 500 or 1,000 watt mercury lamp should be condensed to a roughly parallel beam with a 800 c.c. flask of water about 13 cm. away (centre to centre) and filtered to give the 4,350 or 3,650 Å mercury line. Rather long exposures are necessary.

2. *Photobromination of cinnamic acid.* The arrangement of lamp, cell, etc., may be as above, and experiments may be made both with 3,650 Å and with 4,360 Å. The rate in this reaction is not proportional to the light intensity but to its square root (see Wolfenden, *Numerical Problems in Advanced Physical Chemistry*, Oxford, Problem 96). The light intensity can be varied by interposing a screen of perforated zinc with small holes in the light-path, and the relative intensity and fraction of light absorbed by the reaction mixture in the cell measured with a light meter. Stock solutions of 0.1N cinnamic acid in CCl_4 and of 0.04N bromine in CCl_4 should be prepared. To begin, mix equal volumes of the solutions in the dark (weak artificial light may be used), fill the cell to a mark, pour out (rinsing with CCl_4) into M/5 KI solution and titrate with N/50 thiosulphate. The titration may be performed in the light. This gives the zero reading. Repeat after exposing the cell for varying exposures of a few minutes to the light. Plot an exposure time-titre graph and determine the initial rate of the photoreaction under these conditions. Repeat the measurements reducing (a) the light intensity, (b) the cinnamic acid concentration, and (c) the bromine concentration. From the initial rates express the change as:

$$\text{rate} \propto (\text{absorbed light intensity})^n (\text{cinnamic conc.})^m (\text{bromine conc.})^l.$$

3. *Photo-equilibria.* The purple dye thionine in dilute aqueous solution is rapidly bleached by ferrous ions in sunlight by reduction to a colourless leuco-compound. In the dark the colour is restored by thermal reoxidation to the dye by the ferric ions. The thionine should be about 0.01 gm./l. and the ferrous salt about 1 gm./l., all in about M/50 phosphoric acid.

4. *o-nitrobenzaldehyde changes in light to o-nitrosobenzoic acid.* The crystals first become green owing to the o-nitroso compound existing in solid solution in the green monomeric form. Later the product

separates out in small white crystals of the dimeric form. Under the microscope it can be seen that the rate of change depends on the crystal orientation if polarized light is used. The yellow substance cinnamylidene malonic acid changes in light into a colourless dimer which is a carboxylic acid of cyclobutano.

5. Paper soaked in potassium ferrioxalate solution, after exposure to light, turns blue on development in a solution of ferricyanide. ('Blue-prints'.)

6. A mixture of 40 c.c. alcohol with 60 c.c. of N/10 aqueous dichromate in light gives acetaldehyde and a precipitate of chromic chromate. A little added acid prevents the precipitation, a green chromic solution resulting.

POLARIZATION OF LIGHT SCATTERING AND OF FLUORESCENCE

The substance should be illuminated by a horizontal condensed beam of light polarized with electric vector vertical. It should be examined in a horizontal direction at right angles to this through a Wollaston double-image prism oriented to give one image over the other. A Nicol prism should be interposed between the Wollaston prism and the eye, and turned so that both images are of equal illumination. The Nicol is then turned through an angle α so that the images are again equal. The degree of polarization of the light is then $\cos 2\alpha$.

Scattering: Examine a fine suspension of bentonite; also follow the changes with time in the precipitation of sulphur from a mixture of equal volumes of N/20 thiosulphate and phosphoric acid solution (diluted 100 times from $d = 1.7$). This sulphur sol shows remarkable colour-changes when viewed by transmitted light, varying as the particle size grows.

Fluorescence: Examine a dilute solution of uranin in glycerine; also a similar solution in water. The fluorescence of large crystals of magnesium platinocyanide shows very interesting effects of polarization.

DISPERSION SCATTERING

1. Mix clean powdered glass or silica with a little carbon disulphide and add benzene gradually until red light is just transmitted. View a strong distant light through a layer of the mixture. Wave-lengths shorter than the red are scattered to the side and red light only transmitted. Warming or altering the liquid composition changes the colour which is passed without scattering. Opal effects result from unequal temperature distribution.

2. Shake 20 c.c. glycerine with 20 c.c. of a 2-3 per cent. solution of cellulose nitrate (11 per cent. N) in amyl acetate. Add 10 c.c. of CS_2

gradually with shaking, then more glycerine until rather viscous; then more CS_2 in small amounts until brilliant colours appear. View as above. A similar mixture can be made from glycerine, benzene, and acetone. Dispersion scattering is also shown by crystals of β benzene hexachloride in CS_2 and by ethyl cinnamate partly polymerized by long standing.

COLOURED GOLD SOLS

Add to 100 c.c. water 1 c.c. of 1 per cent. gold chloride solution, 1–3 c.c. of 1 per cent. potassium carbonate solution, and 1–2 c.c. of 0.025 per cent. hydrazine hydrate solution. The colour varies from blue to scarlet depending on the particle size, which again depends on the pH of the solution.

VARIATION OF LIGHT SCATTERING WITH WAVE-LENGTH

Add a little titanium dioxide powder (anastase) as used for paint pigment to water and allow to settle for several days. The very fine particles left in suspension scatter short-wave light much more strongly than long-wave light, and the suspension appears orange by transmitted light.

FLUORESCENT LIQUIDS FOR DEMONSTRATION

Vaseline: bluish-white.

Triphenylmethane in benzene: blue.

β -methyl umbelliferone in water: blue.

Anthracene in benzene: blue.

Aesculin in water: blue.

Acid quinine sulphate in water: blue.

Uranin in water: yellow-green.

Acriflavine in water: yellow.

Rhodamine in water: orange.

Magdala red in alcohol: red.

1, 4-dihydroxyanthraquinone in conc. H_2SO_4 : red.

Chlorophyll solution: red. Made by air-drying stinging-nettle leaves and extracting in the cold with acetone, 80 per cent. by volume.

For the colourless marking of paper, fabric, etc., fluorescing blue in ultra-violet light, use a dilute solution of the sodium salt of amino G-acid.

FLUORESCENT SOLIDS. (Very few solid dyes are strongly fluorescent at ordinary temperature)

Anthracene.

Potassium or ammonium uranyl sulphate.

Lithium, magnesium, potassium, and barium platinocyanides.
Some varieties of fluorspar.

Salicylic acid.

Phthalimide.

6-phenyl 3-carbethoxy α -pyrone.

Natural or artificial rubies.

Activated zinc sulphides. (Silicates and tungstates are fluorescent only at wave-lengths beyond 3,000 Å.)

FLUORESCENT INDICATORS. (For observation in 3,650 Å light)

	pH	Colour change
β -naphthylamine	3.5	Colourless—blue.
3, 6-dihydroxyphthalimide	2.4 and 7	Blue—green—green yellow.
Acridine	5	Green—violet.
Quinine	6 and 9.5	Bright blue—violet—colourless
β -methyl umbelliferone	7	Colourless—blue.

DYE PHOSPHORS

Boric acid is melted on a glass square by heating on a hot plate, and a little finely powdered fluorescein (not Na salt) sprinkled on. When the whole has melted together another heated glass plate is applied and the preparation allowed to cool to a glass. Fluorescein in this state phosphoresces (after exposure) for a few seconds, while the period of fluorescence of the sodium salt in water is only 10^{-8} seconds.

FLUORESCENCE QUENCHING

Dilute solutions of acid quinine sulphate in water have their fluorescence quenched by iodide ions.

For dilute solutions of anthracene in benzene, bromobenzene may be used as a quencher.

'Concentration' quenching may be illustrated by strong and weak solutions of anthracene in benzene and of uranin in water. The effects in the first are due to deactivating collisions giving dianthracene and in the second to polymer formation. (Chap. IV.)

EFFECT OF MEDIUM ON FLUORESCENCE

Expose to Hg light 3,650 Å dilute solutions of dimethylnaphtheturhodine in methyl and ethyl alcohols, acetone, pyridine, benzonitrile, ether, chloroform, benzene, ligroin, and dioxane. The colour and fluorescence vary with the dielectric constant of the liquid except for dioxane, where the dielectric constant is very low because of the molecular symmetry. The phenomenon illustrates the distortion of the dye molecules by the electrical fields of the solvent molecules whereby their energy levels are altered. The dye is made by gradually warming 20 gm. nitrosodimethylaniline hydrochloride and 10 gm. β -naphthylamine in 50 c.c. acetic acid, extracting the product with

aqueous HCl and precipitating with sodium acetate. Purify by dissolving in alcohol containing HCl, evaporate to small volume, and treat with conc. HCl. When the hydrochloride has crystallized, filter off and wash with a little alcoholic HCl. Treatment with aqueous NH_3 gives the free base which is crystallized from toluene. M.P. 205°C .

STREAMING DOUBLE REFRACTION

Grind up 1 gm. of benzopurpurin 4B with a little water and stir the paste into 1 litre of boiling water. After cooling add 70 c.c. or more of 10 per cent. KCl solution. The amount should be just sufficient to make the liquid somewhat turbid, but not enough to coagulate it. View by transmitted light between crossed nicols either when gently stirred in a glass cell 1–2 cm. thick or when flowing down a tube (not so fast as to be turbulent) about $\frac{1}{2}$ cm. bore, preferably with flat sides, and oriented so that the flow is at 45° to the extinction positions of the nicols.

TRIBOLUMINESCENCE

Grind between two test-tubes, one inside the other, or in a mortar with the end of a test-tube any of the following: *p*-acetylaminophenyl salicylate, acenaphthene, sucrose, acid potassium tartrate, uranyl nitrate or acetate, barium bromate or chlorate.

CRYSTALLOLUMINESCENCE

Cool in the dark a filtered hot saturated solution of strontium bromate in water; or a petrol ether solution of menthyl formylphenyl acetate, $\text{C}_6\text{H}_5\cdot\text{CH}(\text{CHO})\cdot\text{COOC}_{10}\text{H}_{19}$.

CRYSTALS AND THE POLARIZING MICROSCOPE

Two microscope slides should be heated, a small amount of the substance placed on one and melted, and the two slides pressed together very tightly and allowed to cool. Very thin layers are necessary for good effects.

1. *Pleochroism*. With one nicol or polaroid above the eyepiece or below the stage examine any of the following, rotating the polarizer or the slide: azobenzene, *o*-nitro phenol, helianthine hydrochloride, copper nitrate, cupric lithium chloride.

2. *Colours of thin crystal plates*. Use two polarizers, crossed, one above and one below; rotate slide or both polarizers together. The crystals may be melted on the slide while under the microscope by the use of a fine gas jet of glass or metal giving a flame 2 mm. high, and the growth of the crystals watched on cooling. The following substances are suitable: naphthalene, benzoic acid, *o*-nitrobenzaldehyde, *o*-nitro-phenol, 2, 4-dinitrophenol, *p*-bromphenol, trichlorphenol,

p-bromaniline, benzophenone, dibenzalacetone, cinnamic acid. Benzoin and 2, 4, 6-trinitro-*m*-cresol give spherulites, and resorcinol and *o*-nitraniline show two solid forms changing one into the other.

3. *Liquid crystals*. Nematic: *p*-azoxyanisole, *p*-methoxy cinnamic acid. Smectic: thallium stearate, ammonium oleate (1 NH₃ per 2 moles oleic acid). Cholesteric: cholesterol esters.

SELECTIVE ABSORPTION BY MERCURY VAPOUR

Mercury lamps are commercially obtainable which contain a rare gas and which emit the bulk of their radiation as the ultra-violet line 2,537 Å. The strong absorption of this line by mercury vapour may be shown with a dish of mercury and a zinc silicate screen, made by dusting willemite or artificial luminescent zinc orthosilicate on a gummy card 1 ft. square. The mercury vapour appears as dark cloud shadows on the luminous screen even at the ordinary temperature, and better with slight warming of the mercury.

CHEMILUMINESCENCE

1. Add calcium silicide (free from excess calcium) gradually to 5 c.c. of conc. HCl. Leave or warm gently to obtain a yellow insoluble silicon derivative. Pour a suspension of this into a large volume of dilute permanganate (in the dark).

2. Make up freshly two solutions: (a) 0.1 gm. *o*-amino phthalic cyclic hydrazide in 1 litre water + 10 c.c. of 2N NaOH. (b) 0.25 gm. potassium ferricyanide + 10 c.c. of 10 vol. H₂O₂ in 1 litre water.

Mix equal volumes. If a little sodium naphthionate is also added and the liquid acidified during the reaction, the light changes from blue to green due to the excitation of the naphthionate fluorescence, which is green in acid solution.

Another method is to dissolve 1 gm. or less of the hydrazide in 100 c.c. of 2N NaOH and add 0.5 c.c. of 10 vol. H₂O₂; then to pour this solution into 1 per cent. hypochlorite solution or into a concentrated alkaline solution of ferricyanide.

3. Dissolve a little white phosphorus in viscous paraffin (medicinal) and pour over the interior surface of a large flask.

DICHROMATISM

Mix a fairly strong aqueous solution of Brilliant Yellow with a weaker one of Brilliant Green. By transmitted light the liquid is red in thick layers, green in thin, and yellow in between.

A solution of methylene green or a mixture of solutions of alkaline litmus and potassium chromate shows a similar effect.

The colour of dichromatic substances is very different in daylight and in artificial light. The gem alexandrite shows this effect.

COLOUR CHANGES IN LIGHTS OF DIFFERENT SPECTRAL DISTRIBUTION

Examine in ordinary white light and in the visible light from a mercury lamp and from a sodium lamp solutions of alkaline phenolphthalein, potassium permanganate, and the dichromatic liquids mentioned above.

Compare the appearances of colour when titrating (in daylight) HCl with NaOH solutions, using as indicator (a) methyl red solution, (b) methyl red + methylene blue solution (0.125 gm. methyl red and 0.082 gm. methylene blue in 100 c.c. 90 per cent. alcohol).

LIMITATION OF THE EYE IN COLOUR DETECTION

Sufficient potassium chromate solution is added to an alkaline solution of litmus so that a layer 1–2 cm. thick can be seen by a spectroscope to transmit red and green only. Using daylight, viewed by transmission, a solution of fairly strong cupric chloride with potassium dichromate, to which a little potassium permanganate is added, can be prepared to match the colour of the first solution very closely. Though the colour match to the eye is close the solutions have very different absorption spectra, the first transmitting red and green and the second yellow. Placed one behind the other they transmit no light. The colour match is greatly disturbed by employing different thicknesses of the solutions or by using artificial light instead of daylight.

COLORIMETRIC CHEMICAL ANALYSIS

The following solutions are useful for the preparation of colour standards:

1. Mixtures of M/4 copper sulphate, M/4 cobalt chloride, and M/6 ferric chloride, all in N/3 HCl.
2. Mixtures of M/100 aquapentammine cobaltichloride, M/100 copper sulphate, and M/500 ammonium dichromate, all in N ammonia solution.
3. Mixtures of N/100 dichromate and N/1,000 permanganate.

Such mixtures must be calibrated against known concentrations of the substance to be determined, using always white light of the same spectral distribution.

IRIDESCENT CRYSTALS OF POTASSIUM CHLORATE

Dissolve 500 gm. of KClO_3 in 1 litre of boiling water and cool slowly in a 'hay-box' or large Dewar. Drain off the cold liquor and examine the crystals in front of a good light. Small flat iridescent crystals may be picked out and mounted in Canada balsam. Sometimes larger crystals up to 1 cm. side may be found. Their colours are faint and not easy to recognize at first owing to surface reflection, but when they are mounted with a black paper background in balsam in a cell

on a glass slide, with a cover-glass set at an angle to throw surface reflection to one side, the iridescent colours, varying with incidence angle, are very vivid. The effects arise from multiple reflections from a large number of parallel 'thin plates' caused by twinning.

SELECTIVE REFLECTION

Crystals of methyl violet and of other dyes show strong selective reflection. The dye may be deposited on glass by evaporation of an alcoholic solution. The reflected colour varies according to the nature of the surface, as crystal air or crystal glass, owing to refraction effects, and is therefore not simply equivalent to the light most strongly absorbed (p. 28). Crystals of magnesium platinocyanide have a brilliant green surface colour on the sides and a violet colour at the ends due to selective reflection. Somewhat similar effects are shown by crystals of dimethylnaphtheurhodine.

GELATINE FILM FILTERS between plate glass or optically worked glass sheets are obtainable commercially. The following are useful examples of Ilford filters.

1. *Filters cutting off shorter wave-lengths.* The limits given are those where the transmission is reduced to about 1 per cent.; 50 per cent. transmission occurs at about 300 Å longer wave-length.

<i>Filter No.</i>	<i>Limit Å</i>	<i>Filter No.</i>	<i>Limit Å</i>
207+813	7,400	202	5,500
207	7,200	201	5,380
609	6,520	111	5,200
206	6,330	110	5,050
608	6,200	109	4,820
205	6,050	108	4,580
204	5,720	102	4,100
203	5,650	809+805	4,050
808	5,570	805	3,750

2. *Filters cutting off longer wave-lengths.* The following transmit the visible from yellow to blue and cut off the red.

<i>Filter No.</i>	<i>Percentage transmission</i>	
	5,800	6,400 Å.
802	42	11
803	35	6.3
804	20	1

3. *Filters isolating spectral bands.* The limits given are those of 1 per cent. transmission.

<i>Filter No.</i>	<i>Maximum transmission</i>		<i>Limits, Å</i>
	<i>Wave-length</i>	<i>Percentage</i>	
304	4,300	50	3,700–5,100
306	4,300	28	3,850–4,950
601	4,300	29	3,850–4,700
806 + 805 + 809	4,500	16	Isolates Hg blue
602	4,700	14	4,450–4,950
303	4,800	65	4,250–5,650
603	4,900	12	4,750–5,200
604	5,200	10	5,000–5,410
407	5,200	60	4,450–6,100
404	5,300	60	4,800–6,100
408	5,300	46	4,850–5,900
807	5,300	22	Isolates Hg green
605	5,500	5.5	5,300–5,750
606	5,800	7.2	5,550–6,100
607	6,000	27	5,780–7,300
808	5,900-red	89	Isolates Hg yellow

Liquid filters are the most flexible and efficient, but are often mechanically undesirable. Gelatine filters can serve most purposes, having good transmission with sharp cuts. Glass filters have the advantage of the greatest stability and invariance to temperature, but usually have flatter transmission characteristics and cannot be obtained with as many variations of transmission as the other filters.

FLUORESCENT SCREEN FOR THE ULTRA-VIOLET

For the focusing of ultra-violet spectrometers a fluorescent screen is helpful. A useful material is anthracene with one part in a hundred or so of naphthacene. The latter hydrocarbon makes the fluorescence green and more brilliant; pure anthracene may also be used, giving a blue fluorescence.

About 10 c.c. of a boiling strong solution of the hydrocarbons in acetone is poured with stirring into about 50 c.c. of a warm solution of gelatine in water. A finely divided precipitate is thrown down. The liquid is poured in a (not too thin) layer on a warmed photographic plate which has been cleaned of its emulsion by boiling in alkali and washing. After warming on a hot plate and allowing to set, the screen is complete. The prepared surface should of course face the light source, and the fluorescence is visible through the back. For work in the far ultra-violet the gelatine may be omitted; some skill then being required to produce a uniform coating.

Another suitable substance is finely powdered uranyl ammonium fluoride.

POLARIZATION IN THE ULTRA-VIOLET

Use a Wollaston or Rochon prism cemented with glycerine.

The following experiments are due to Professor H. W. Melville, F.R.S.

FLUORESCENCE QUENCHING

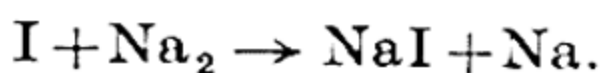
Focus light from a sodium lamp on to an evacuated Pyrex bulb containing some sodium, which is uniformly heated to about 200° C. by bunsen burners. Fluorescence of the *D* lines is excited throughout the bulb. Interpose a second similar heated bulb; the fluorescence in the first is weakened by light absorption in the second. Replace the second bulb by one containing 10 mm. of hydrogen in addition to sodium. On heating this the fluorescence in the first bulb is weakened as before, but only feeble fluorescence appears in the interposed bulb, owing to the quenching process:



The lifetime of Na^* is about 10^{-7} second, and the above collisions take place every 10^{-8} second.

CHEMILUMINESCENCE

A Pyrex tube with side tube is sealed off at one end and the glass pushed in to form an internal point. A small evacuated bulb of iodine is then introduced. Some sodium is placed at the other end, which is sealed, and the tube evacuated through the side tube; the sodium being melted to drive off or to consume volatile material. The tube is now sealed off from the pump. To excite the chemiluminescence the iodine bulb is broken by allowing it to fall against the internal point, and the iodine end gently heated while the sodium end is strongly heated. Where the vapours meet strong *D* line luminescence appears and sodium iodide is deposited:



The light results from collisions between the freshly formed NaI molecules of high energy and sodium atoms, the energy being transferred to the latter which quickly radiate their characteristic atomic lines. (See *Proc. Roy. Inst.* 1938, vol. xxx, No. 141, p. 363.)

TABLE OF CONSTANTS, ETC.

1 joule = 10^7 ergs.

1 calorie = 4.185 joules.

1 watt = 1 joule per sec. = 10^7 ergs per sec.

1 μ = 10^{-4} cm.; 1 m μ = 10^{-7} cm.; 1 Å = 10^{-8} cm.

c. Velocity of light *in vacuo* = 2.99776×10^{10} cm. per sec.

h. Planck's constant = 6.624×10^{-27} erg sec.

e. Electronic charge = 4.803×10^{-10} absolute electrostatic units
= 1.602×10^{-20} absolute electromagnetic units.

m. Electron mass = 9.11×10^{-28} gram.

M_{O₁₆}. Mass of O¹⁶ atom = $16 \times 1.660 \times 10^{-24}$ gram.

N. Number of molecules in one gram molecule = 6.023×10^{23} .

k. Boltzmann's constant = 1.3805×10^{-16} erg per degree per molecule.

R. Gas constant for one gram molecule
= 8.314×10^{-7} ergs per degree per gram molecule,
= 1.986 calories per degree per gram molecule.

1 electron per second = 1.6×10^{-19} amp.

1 erg = 4×10^{12} quanta at 5,000 Å.

Atomic dimensions $\approx 10^{-8}$ cm.

Colloidal particles $\approx 10^{-7}$ – 10^{-5} cm.

Wave-length, middle of visible spectrum $\approx 5 \times 10^{-5}$ cm. = limit of the microscope.

Total number of collisions per c.c. per second between two molecules *A* and *B* at pressures *p_A* and *p_B* mm. Hg.

$$= p_A p_B (d_A + d_B)^2 \left(\frac{M_A + M_B}{M_A M_B} \right)^{\frac{1}{2}} T^{-\frac{1}{2}} \times 10^{42},$$

or for one kind of molecule, $p^2 d^2 M^{-\frac{1}{2}} T^{-\frac{1}{2}} \times 3 \times 10^{42}$, where *M* is the gram molecular weight and *d* = molecular diameter (cm.).

Average time between collisions of a molecule of gas at N.T.P.
= 10^{-10} sec.; for a liquid = 10^{-12} sec.

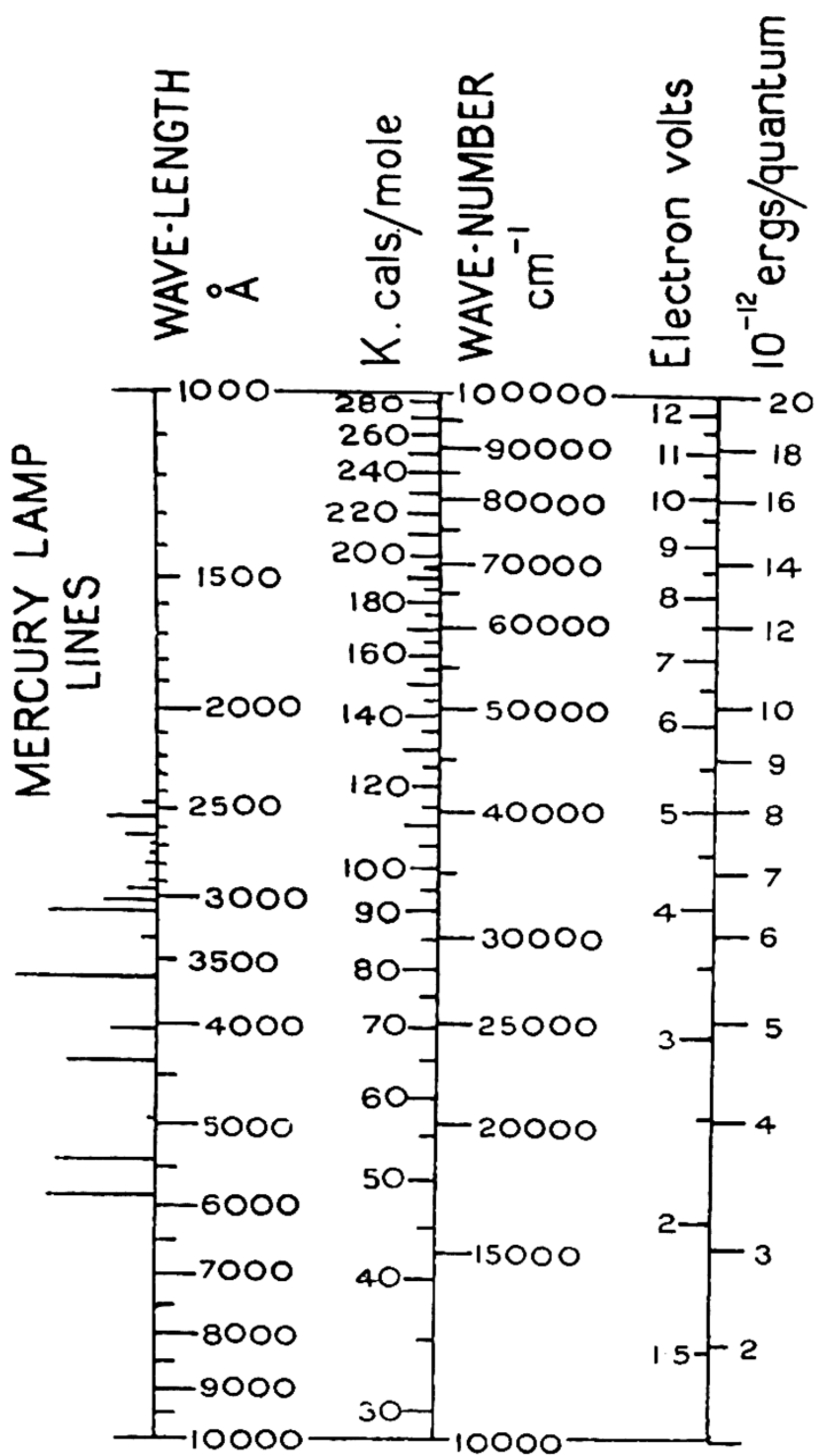


FIG. 59. Energy conversion chart.

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